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# FACTORS AFFECTING ELECTROPHORETIC DEPOSITION OF $\beta$ - $\beta''$ ALUMINA TUBES

By

ASHOK B. MALAGE

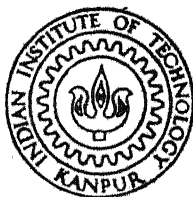
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DEPARTMENT OF METALLURGICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR  
JANUARY, 1980

# **FACTORS AFFECTING ELECTROPHORETIC DEPOSITION OF $\beta$ - $\beta''$ ALUMINA TUBES**

A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of  
MASTER OF TECHNOLOGY

By  
ASHOK B. MALAGE

4128

to the  
DEPARTMENT OF METALLURGICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR  
JANUARY, 1980

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## CERTIFICATE

Certified that this work on "Factors Affecting Electrophoretic Deposition of  $\beta$  -  $\beta$ " Alumina Tubes" by Ashok B. Malage has been carried out under my supervision and that this has not been submitted elsewhere for a degree.



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## ACKNOWLEDGEMENT

I shall ever remain deeply indebted and extremely grateful to Prof. E.C. Subbarao who has guided throughout this work and without whose invaluable inspiration and encouragement the investigation contained in this thesis would not have been possible.

My thanks are to all my friends who made my stay in the Campus a memorable one.

Thanks are to Sri S.S. Seghal, B. Sharma, V.P. Gupta, R.S. Mishra and R.N. Srivastava who helped in different phases to get the thesis in the present form.

I am very much thankful to Sri Viswanath Singh for his help in all phases of the work.

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## ABSTRACT

Kinetic equations of electrophoretic deposition were verified quantitatively using dry distilled isoamyl alcohol vehicle for  $\beta$  -  $\beta$ " alumina suspensions, as deposition yield with respect to concentration (40-60 g/100 ml) applied voltage (50-500 V), deposition time (0-50 seconds) and electrode separation (0.5-1.5 cm). Number of methods have been studied to produce thin walled  $\beta$  -  $\beta$ " alumina tubes for Na/S battery by using electrophoretic deposition as a forming technique. Thin tubes over wax skeleton were produced with this technique. Both negatively and positively charged particles were also deposited over the stainless steel mandrels and study was made for easy removal of the deposits.

## CHAPTER I

### INTRODUCTION

#### I.1 Need for Stored Energy

The demand for energy is increasing day by day with variety of utilization, preferably in electrical form. The conventional energy sources are getting exhausted due to excess usage, and a thought must be given to explore alternative sources, simultaneously using the available energy in a more economic way.

While research is going on for developing alternative sources of energy, its storage cannot be neglected. When sources are such that generation is not possible for all 24 hours of the day (e.g. solar, wind, tidal energy etc.), an efficient storage system finds its importance. The conventional energy sources are to be used economically whenever needed by avoiding fluctuations, using stored energy. Hence, in order to have optimum economic use of energy, an efficient storage is necessary.

Stored energy can be used mainly for the following purposes viz., load leveling, rural applications and in electrical vehicles.



### I.1.A Load Leveling.

Demand for electricity varies from season to season and even hour to hour. Power plants must have generating equipment available for the times of peak electrical consumption such as daylight hours during week days.

Peaking turbines are used to supplement generating capacity during times of high demand. Such turbines have the advantage of being able to come on line quickly, but they are expensive to operate, and normally are fueled by natural gas. Power plants have to reduce large fluctuations (Figure I.1) that occur in electricity demand at any instant. One important way of load leveling, or reducing the peaks, would be to run large base load power plant generators continuously at their most efficient levels even during low demand periods, store the excess electricity which is then used during periods of higher demand. Since base load plants are usually nuclear or coal fired, this practice would tend to shift fuel dependency away from oil and natural gas needed for peaking turbines. The concept of producing energy at low cost, storing it in idle time and utilizing the same when required is called load leveling.

### I.1.B Rural Application.

The power needed by villages and remote places is very small. The typical use of power in a village is

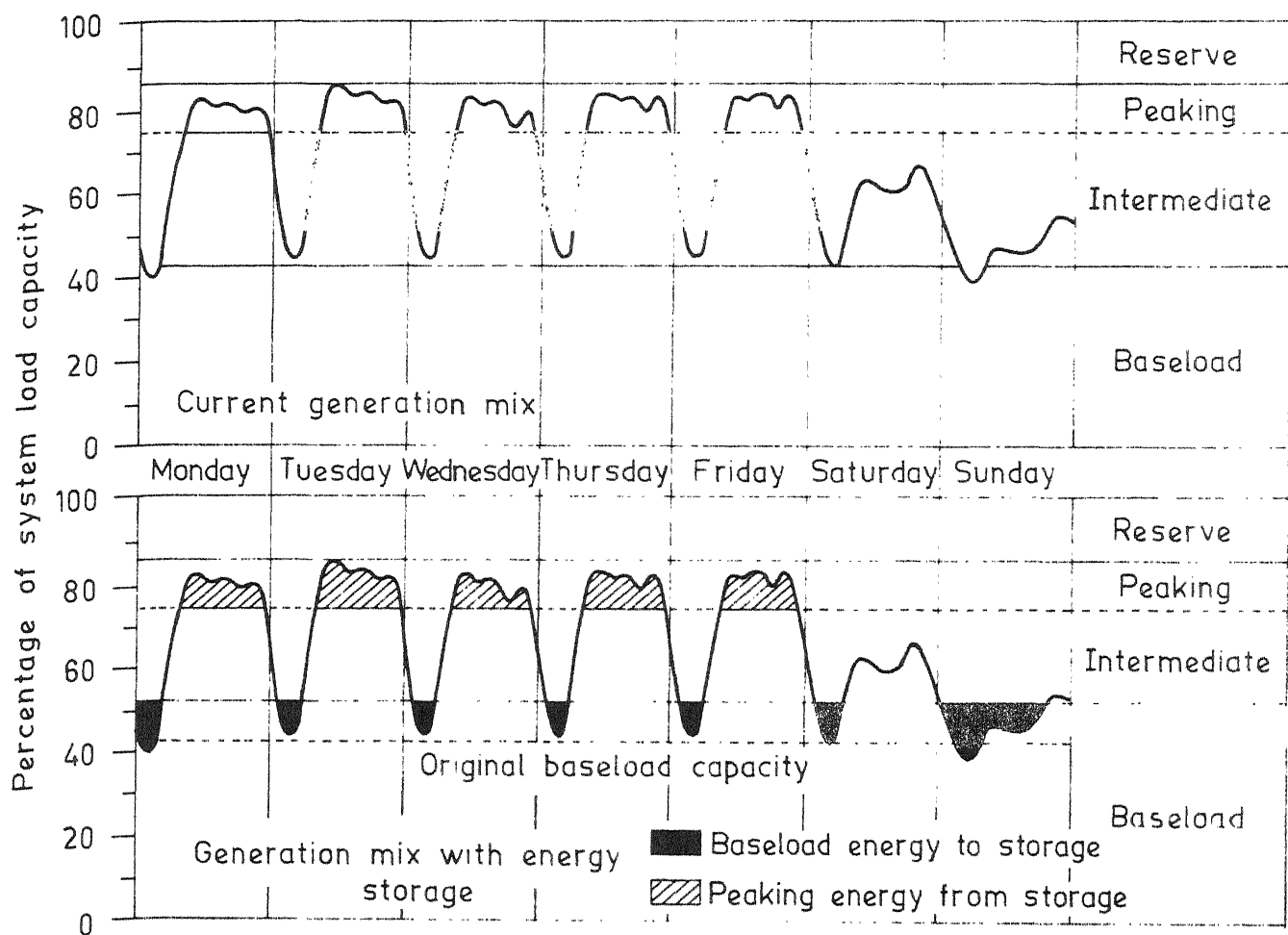


Fig. I.1 Typical weekly load curve of an electric utility ,  
 generation for load with storage and no storage .  
 (Ref. 1)

about 1 unit per day per house. The cost of supply (transmitting) is more than the production since the utility points are scattered. Transmission losses are more at low voltage, hence it should be supplied at high voltage for low demand which is not economic. In such cases, the power can be stored and distributed to remote places according to the demand. The exhausted storage units can be brought back to central point, recharged and can be supplied again.

#### I.1.C Electric Vehicles.

Electric vehicles use stored electricity to drive an electric motor for propulsion. The conventional vehicles use gasoline which causes air pollution and creates noise. The increase in gasoline prices have renewed interest in electric vehicles.

Since electric vehicles do not have combustion engines, they are quiet running and do not burn gasoline. They can reduce air pollution problems in cities, because their source of energy could be fueled by storing electricity or replacing the storage unit. This shifts the fuel source to the central station power plant which uses coal or nuclear power.

However, at present electric vehicles have the disadvantages of relatively slow acceleration, low speeds and limited distance between charging.

## I.2 Modes of Energy Storage.

In the absence of a practical system for direct storage of electricity, storage is accomplished by conversion of electricity to some other form of energy which can be reconverted to electricity as needed. There are several ways of storing electrical energy viz. mechanical, thermal or electrochemical. The storage system or mode of storing energy depends on the particular needs. Some times it may be the combination of the above systems.

Mechanical storage system consists of storing pumped hydro, compressed air or fly wheel. In pumped hydro system, electricity is used to pump water into elevated reservoirs, during periods of low electricity demand. The potential energy in the stored water is recovered and reconverted to electricity in the hydroelectric plant during peak demand periods. This system involves high capital cost, geological problems of elevation and stability, and takes long time to operate. The energy stored in the form of compressed air is used to convert to electrical form by operating a turbine. The problem arises because of the storage of air. Rock holes or mines can be used for storing of compressed air, but these have to withstand the release and compression of pressure simultaneously. In fly wheel, the stored energy is released by allowing it to rotate. Materials that withstand the stresses at

circumference are used, since stresses are at circumference. So, highly anisotropic materials are to be used. Fly wheel has less efficiency due to friction and its weight. Hence to minimise friction, bearings should be used and operated in vacuum, if possible.

In thermal storage system, the sensible heat is used to store energy as high pressure steam, and used as required. The problems associated with this are using proper high strength, non corrosive containers, but these are very costly. In super conductors, energy can be stored in electrical form and can be given out again in electrical term. This requires very low temperatures (liquid He temperature).

In chemical storage, energy can be stored in two forms by chemical means, viz., (i) storage of hydrogen and (ii) storing of electricity in batteries. Hydrogen can be stored in solid materials like rare-earth compounds, e.g.  $\text{LaNi}_5$ . It is stored in the form of hydrides and hydrogen can be released and used as required. These materials have to have the ability to adsorb and desorb. This type of storage is used mainly in defence applications and air craft.

In the case of batteries, energy can be stored in electrical form and can be taken out in electrical form, hence no further conversion is required. It is instantaneously

available. It is of module construction, and depending on the use, modules can be modified by arranging a number of batteries. This is a portable unit, and no transmission is required and hence can be installed at any place.

The disadvantages of the battery systems are:

- (i) produces d.c. hence requires d.c.-a.c. converters.
- (ii) storage is small, and to have large amount of energy, the unit becomes bulky.
- (iii) chemicals used are corrosive and toxic.

Compared to other storage devices, batteries can be used upto certain time (hours) and after that they should be recharged.

The general characteristics of these battery systems are long life, capability to withstand large number of charge-discharge cycles and almost instantaneous charging and discharging (relatively low polarization) capacity.

### I.3 Comparison of Electrochemical Storage Batteries.

Table I.1 gives a list of reversible storage systems which utilize electrochemical energy for their operation. Each type has its own merits and demerits. For example, lead-acid battery has low energy density, low current density, high cycle life but active material cost is high.  $\text{Zn/Cl}_2$ ,  $\text{Na/SbCl}_3$  have low current density,  $\text{LiSi/FeS}_2$  has low current density and high operating

Table I.1

Characteristics of some high energy density battery systems (2, 3)

System	Operating Temperature °C	Theoretical Energy Density Wh/kg	Practical Density Wh/kg	Practical Energy Density Wh/cm <sup>3</sup>	Current Density mA/cm <sup>2</sup>	EMF V	Size/ KWh	Life Cycles	Active Material Cost \$/ KWh
Pb/PbO <sub>2</sub>	20-30	242	19.8	0.04574	10-15	1.9	>20	>2000	8.5
Na/s	300-350	792	154.0	0.1524	90-100	1.08	0.03	1000	0.50
Na/SbCl <sub>3</sub>	200	770	110.0	0.1220	42	2.4	0.02	350	2.35
LiSi/FeS <sub>2</sub>	400-450	946	187.0	0.2134	35-45	1.4	0.1-0.3	1000	4.27
Zn/Cl <sub>2</sub>	50	462	55.0	0.04269	40-45	1.9	1.4	250	0.91

temperature compared to Na/S battery. From the table it appears that though Na/S cell requires  $\sim 300^{\circ}\text{C}$  for its operation, it has quite a few attractive features. It has higher current density and higher energy density (except  $\text{LiSi/FeS}_2$  which operates at  $400\text{--}450^{\circ}\text{C}$ ).

The high density batteries like Na-S batteries, differ from lead acid batteries in improved energy density, and use of cheaper materials. Figure I.2 shows the importance of high energy batteries with respect to cost and operation time. The relative over all economy of different modes of power generation depends on annual hours of operation. For peaking services battery storage has the advantage of low capital cost. So, it is evident that high energy density batteries are strong candidates for energy storage and Na-S battery is one of them.

#### I.4 Sodium-Sulfur Cell.

A typical Na-S cell is shown in Figure I.3. Liquid sodium and liquid sulfur are used in this L/S/L cell as anode and cathode respectively. The electrolyte in the cell is  $\text{Na}^+$  ion conducting  $\beta - \beta''$  Alumina. It is possible to use tubular as well as flat plate forms of  $\beta - \beta'' \text{Al}_2\text{O}_3$  electrolytes. A tubular shape can be used in case of high energy capacity whereas flat plate is advantageous in high power application. The tubular shape electrolyte acts as



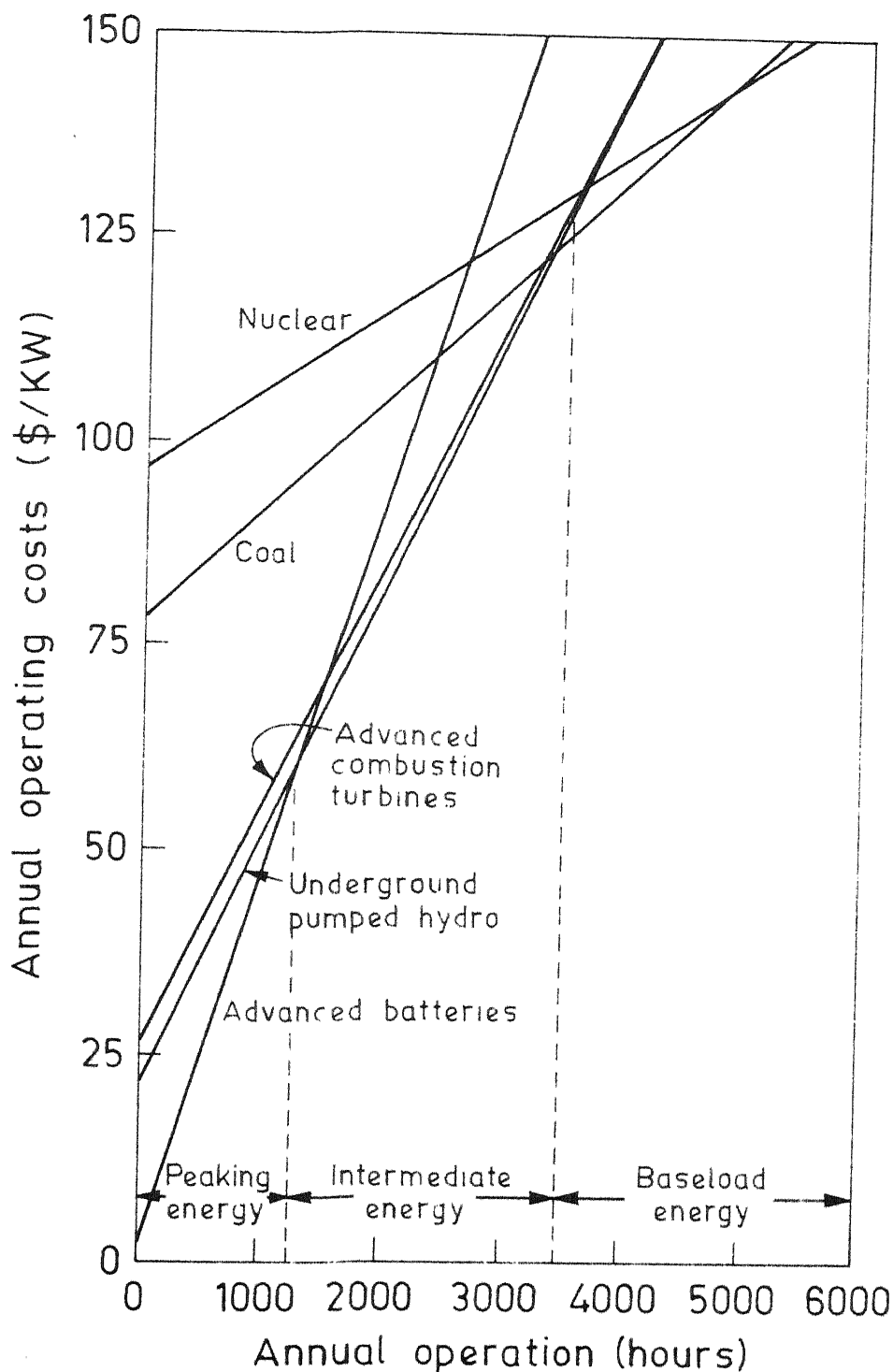


Fig. I.2 Comparison of advanced batteries with other energy sources. (Ref. 4)

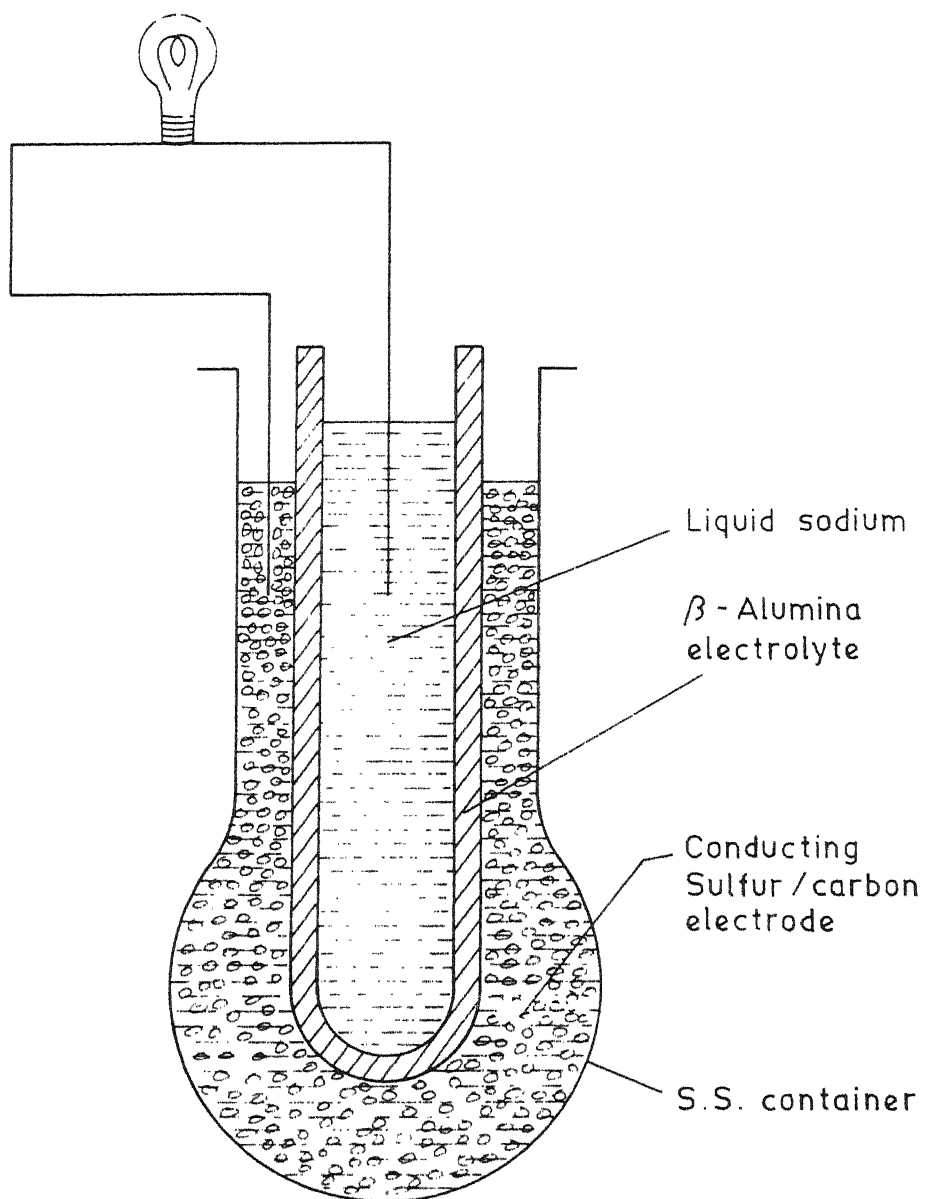
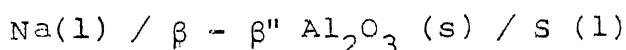
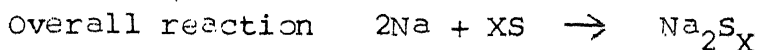
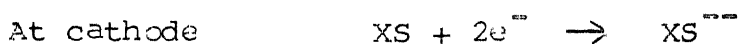
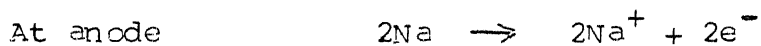


Fig. I.3 Sodium - sulfur cell . (Ref. 5)

a container for sodium anode and is immersed in molten sulfur as shown in Fig. I.3. The cathode material is graphite felt impregnated with sulfur, since sulfur itself is a non conductor. The stainless steel outer container serves as the cathode current collector. The principle of Na-S cell is as follows:



In operation, when electric cell discharges through an external circuit, the liquid sodium in contact with solid electrolyte is ionized, with release of electrons and form the corresponding positive  $\text{Na}^+$  ions. The electrons leave the cell through the negative terminal to external circuit, while the  $\text{Na}^+$  ions are conducted through solid electrolyte ( $\beta - \beta'' \text{Al}_2\text{O}_3$ ) to the liquid sulfur. The electrons from the external circuit are eventually conducted by current collector and through the graphite felt to the liquid sulfur forming negative sulfur ions, which in turn combine with  $\text{Na}^+$  ions to form polysulfides.



$$E_{300^\circ\text{C}} = 2.08 \text{ V.}$$

In the first stage of discharge, the compound  $\text{Na}_2\text{S}_5$  is formed giving a constant open circuit voltage (OCV) of 2.08 V. On further discharge, lower polysulfides are formed (e.g.  $\text{Na}_2\text{S}_4$ ), but the discharge can be carried as far as  $\text{Na}_2\text{S}_3$ . Beyond this point the polysulfide melting point starts to rise rapidly. Usually this battery is operated at  $300^\circ\text{C}$ , and further discharge would lead to freezing of the cathode material.

To recharge the electric cell, a current is provided to feed electrons through negative terminal to liquid sodium. The polysulfides dissociate and the  $\text{Na}^+$  ions released flow through solid electrolyte to liquid sodium chamber and the ions neutralise and mix with the sodium present. Thus once again this can be used in discharge mode.

Several problems in these processes are under investigation. Some of them are: sodium anode, electrolyte, sulfur cathode and seals. Among all these, electrolyte is very important which determines the cell reaction and hence the output energy. A good electrolyte is characterized by its low electrical resistance, high strength and high density. Since the electrolyte separates fluids which explode if they come in direct contact, the mechanical soundness of the electrolyte membrane becomes very important. Recent studies suggested that 80% of the cost of the batteries

and 60% of the failures may be attributed to electrolyte. Therefore, production of dense, mechanically strong, ionically conducting  $\beta - \beta''$  - alumina shapes (as closed end tubes) is receiving the attention of many investigators.

### I.5 Structure and Properties of $\beta - \beta''$ - Alumina.

#### I.5.A $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ System.

The compounds of  $\beta$ -Alumina type which are ternary oxides of general formula  $\text{Na}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$  ( $\text{A}^{3+} = \text{Al}^{3+}, \text{Fe}^{3+}$ ,  $\text{B}^+ = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Ag}^+$  etc.) constitute an important group of materials belonging to the superionic conductors. The high ionic conductivity is due to the diffusion of  $\text{B}^+$  ions in loosely packed planes of the structure.

Sodium  $\beta$ -alumina is a general term that refers to a family of sodium aluminates with closely related structures and chemical properties. First it was identified as an allotropic form of alumina, but it soon became evident that  $\beta\text{-Al}_2\text{O}_3$  belongs to the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$  system. Several types of phase diagrams have been proposed. Figure I.4, shows the phase diagram plotted by Fally et al<sup>(6)</sup>. For alumina greater than 84 mole per cent  $\text{Al}_2\text{O}_3$ , two stable phases appear in  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$  system.

- (i) The sodium aluminate ( $\text{NaAlO}_2$ ) in three allotropic forms  $\beta$ ,  $\gamma$  and  $\delta$ .

(ii) The  $\beta$ -alumina, a nonstoichiometric phase of composition between  $5.33 \text{ Al}_2\text{O}_3 \cdot \text{Na}_2\text{O}$  and  $8.5 \text{ Al}_2\text{O}_3 \cdot \text{Na}_2\text{O}$ . The domain increases from  $1050^\circ\text{C}$  to  $1400^\circ\text{C}$  and then decreases on the side rich in  $\text{Na}_2\text{O}$ . The domain disappears around  $2000^\circ\text{C}$  at a peritectic point where the composition is about  $8.5 \text{ Al}_2\text{O}_3 \cdot \text{Na}_2\text{O}$ . The two phases ( $\text{NaAlO}_2$  and  $\beta\text{Al}_2\text{O}_3$ ) are separated by an eutectic at  $1580^\circ\text{C}$ .

In  $\beta - \beta''$  - alumina domain of coexistence (shaded area in Figure I.4) for the same temperature and same heat treatment, the proportions of  $\beta$  (stable) to  $\beta''$  (unstable) practically do not vary as the amount of alumina varies. (6a) However  $\beta''$ -alumina can be stabilized by the introduction of impurities like  $\text{Mg}^{2+}$  or  $\text{Li}^+$  ions. The introduction of impurities also modify the electrical conductivity of the final sintered products. (7)

$\beta - \beta''$  - alumina is prepared by solid state reaction between  $\alpha$ -alumina and sodium carbonate taken in stoichiometric preparation at temperatures above  $1050^\circ\text{C}$ . Ray et al (8) have identified some problems involved in synthesis of  $\beta$ -alumina, such as segregation and  $\text{Na}_2\text{O}$  loss. The phases were studied by X-ray diffraction. Also, they stabilized  $\beta''$ -alumina by  $\text{MgO}$  and  $\text{Li}_2\text{O}$  addition in different ratios.

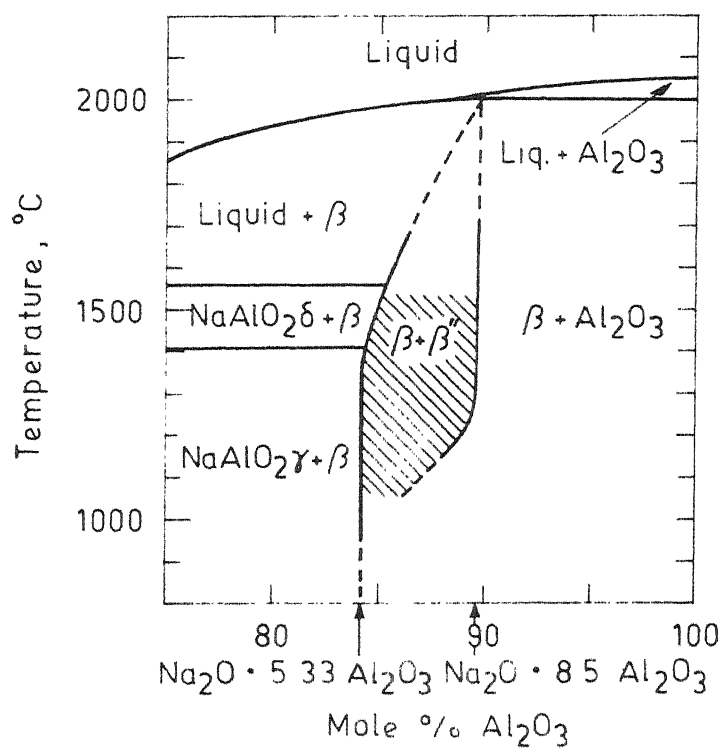


Fig. I.4  $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3$  system (Ref. 6)

### I.5.B Structure of $\beta$ - and $\beta''$ - Alumina.

X-ray diffraction is used for determining the crystal structure. Beevers and Ross, in 1937, established the basic crystal structure of  $\beta$ -alumina. It belongs to the hexagonal system and consists of  $[\text{NaO}]$  layer and  $[\text{Al}_{11}\text{O}_{16}]$  blocks stacked alternatively. The blocks of  $\text{Al}^{3+}$  and  $\text{O}^{2-}$  are packed in the same fashion as the packing in  $\text{MgAl}_2\text{O}_4$  spinel, and are called 'spinel blocks'.  $\text{Al}^{3+}$  ions occupy octahedral sites as well as tetrahedral sites occupied by  $\text{Mg}^{2+}$  in spinel. These spinel blocks are separated by loosely packed  $[\text{NaO}]$  layer. Because of the loose packing, space is available for the movement of  $\text{Na}^+$  ions, leading to a high ionic conductivity. Conductivity is limited to only the  $[\text{NaO}]$  plane and along c-axis, conduction is very difficult. Therefore the material is highly anisotropic.

In  $[\text{NaO}]$  layer,  $\text{O}^{2-}$  ions are packed loosely, leaving many available sites for  $\text{Na}^+$  ions and only some of them are actually occupied by  $\text{Na}^+$  ions, and the remaining sites are left vacant designated by (b) and (c) in Figure I.6.

The conduction plane of  $\beta$ -alumina is a mirror plane and thus the fcc packing arrangement of the oxide ions reflects from the mirror plane (Figure I.5). In  $\beta''$ -alumina this packing arrangement is slightly different, as the conduction plane is not a mirror plane. As shown in



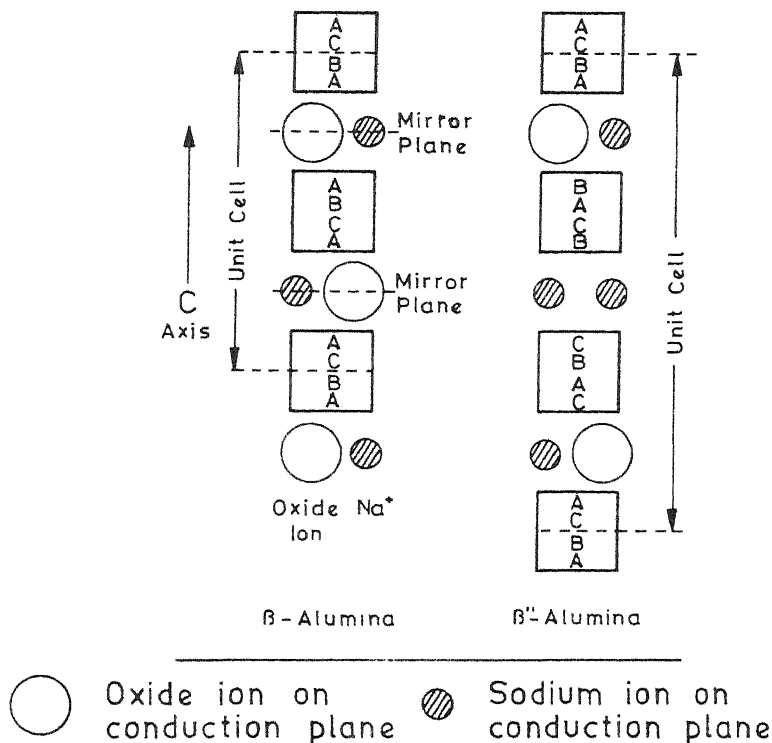


Fig. I.5 Oxide ion packing arrangement in  $\beta$  and  $\beta''$  alumina (Note : letters refer to stacking arrangement where ABC represents face - centered cubic packing while ABAB would represent hexagonal packing) [Ref. 9]

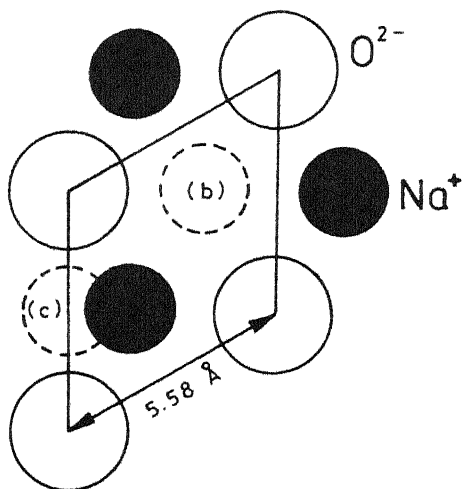


Fig. I.6 Arrangement of ions in the  $[\text{NaO}]$  layer. (Ref. 10)

Figure I.5, there are 3-spinel type blocks before the stacking arrangement is repeated; for this reason,  $\beta''$ -alumina is called '3-block' material while  $\beta$ -alumina is called '2-block' material. The additional conduction planes lead to hexagonal crystal structure for  $\beta$ -alumina and rhombohedral structure for  $\beta''$ -alumina. The lattice constants and other physical properties of  $\beta$  and  $\beta''$  alumina are given in Table I.2. The conductivity of  $\beta''$ -alumina is greater than that of  $\beta$ -alumina, due to the presence of one extra NaO plane.

#### I.6 Forming of $\beta$ - $\beta''$ Alumina Electrolytes.

The manufacturing problems of  $\beta$ -alumina have proved to be much more severe than for comparable ceramic materials and also because the performance and durability of the ceramic in cell is sensitive to its microstructure and composition. These problems are largely defined by volatility of sodium oxide at elevated temperatures which is required for conventional sintering techniques above  $1400^{\circ}\text{C}$ . In common with other ceramic materials,  $\beta$ -alumina is manufactured by sintering a consolidated powder in solid state.

Green body of  $\beta$ -alumina is prepared by different techniques viz., isostatic pressing<sup>(12)</sup>, extrusion<sup>(12)</sup>, slip costing<sup>(13-13a)</sup> and electrophoresis.<sup>(6, 14-17)</sup>

Table I.2  
Properties of  $\beta$ - and  $\beta''$ -alumina

	$\beta$ -Alumina	$\beta''$ -Alumina
(a) Composition	$\text{Na}_2\text{O} \cdot 11 \text{Al}_2\text{O}_3$	$\text{Na}_2\text{O} \cdot 5 \text{Al}_2\text{O}_3$
Lattice parameter	$a = 5.5 \text{ \AA}$ $c = 22.52 \text{ \AA}$	$a = 5.58 \text{ \AA}$ $c = 33.95 \text{ \AA}$
Density	$3.24 \text{ g/cm}^3$	$3.27 \text{ g/cm}^3$
(b) Electrical properties <sup>(11)</sup>		
	Ionic Reactivity ( $\sigma$ )	Activation Energy ( $E_a$ )
$\beta\text{-Al}_2\text{O}_3$ (single crystal)	$0.5 \text{ } \mu\text{m}$ (575 K)	13 kJ/mol
$\beta\text{-Al}_2\text{O}_3$ (poly crystal)	$0.12 \text{ } \mu\text{m}$ (575 K)	24 kJ/mol
$\beta''\text{-Al}_2\text{O}_3$ (single crystal)	$0.01 \text{ } \mu\text{m}$ (575 K)	13 kJ/mol
$\beta''\text{-Al}_2\text{O}_3$ (poly crystal)	$0.05 \text{ } \mu\text{m}$ (575 K)	20 kJ/mol

Isostatic pressing<sup>(12)</sup> is a simple technique in which powders contained in a shaped rubber bag with a steel mandrel are compacted by applying a hydraulic pressure ( $150-400 \text{ MN/m}^3$ ) to the outside of the bag. The powder is compacted isostatically to a high density and good dimensional tolerance is achieved. Closed end tubes with thin walls and lengths over 500 mm can be fabricated and for wall thickness  $< 1 \text{ mm}$ , the green shapes can be machined. The principal requirement for isostatic pressing in large quantities is a free flowing powder that will fill the mold cavity with reproducible quantity of powder. This requires pressure chamber and other auxiliary units.

Extrusion<sup>(12)</sup> is potentially a very cheap method of making large quantities of open-ended  $\beta$ -alumina tubes, but there are problems in the development of a suitable binder system to permit rapid extrusion with moderate forces. Binder systems consisting of polyvinyl pyrrolidane and ethylene glycol with small additions of colloidal fibrillar hydrated alumina have been shown to be effective, although extrusion forces were high and sintered densities were moderate. In this case, closing one end of the tube is a problem. This requires a pressure unit and other auxiliary huge set ups.

Tubes can be fabricated by slip casting in both aqueous<sup>(13)</sup> and non aqueous<sup>(13a)</sup> medium. Water leaches the

sodium from the  $\beta$ -alumina with increasing pH and finally results in the formation of gels. Methanol gave good results<sup>(13a)</sup>, though traces of moisture present, tend to adsorb the particles to form gels. Hence, the use of dry powder and dry methanol is recommended. Here, the shrinkage is very small and the tube formed sticks to the wall of the mold, and becomes difficult to be removed. River et al<sup>(13a)</sup> could slip cast the tubes in methanol medium, using alumina powder molds. The electrical resistivity reported<sup>(14)</sup> in a direction across the tube is  $\approx 50 \text{ } \Omega\text{-cm}$  at  $300^\circ\text{C}$ .<sup>(13a)</sup>

Electrophoretic deposition<sup>6,14-17)</sup> uses an electrically charged mandrel placed in a suspension of  $\beta$ -alumina in a suitable dielectric liquid. When an electric field is applied between the mandrel and a suitable counter electrode, the powder is deposited uniformly on to the mandrel to build desired thickness. Removal of deposit from the mandrel is some times difficult. This is a very easy technique which takes a short time. The deposit thickness can be controlled by voltage or time. Hence it is a versatile process for ceramic fabrication.

Since both electrical as well as the mechanical properties of  $\beta$ -alumina are very anisotropic, polycrystalline ceramic fabrication is difficult with more conventional processing techniques. The electrophoretic deposition gives desired good deposits; hence it is possible to produce closed end tubes.

## I.7 Electrophoresis.

The phenomenon of electrophoresis has been known since 1809 with the work of F.F. Ruess. The introduction of double layer concept by H. van Helmholtz for explaining the mobility of the particles has enabled this technique to be used in different fields, viz., biochemistry, medicine and in paint technology.

The advanced research in this area enabled the use of this technique mainly as a coating and as a forming method. Electrophoretic deposition of ceramic powders is of more recent origin. Avgustinik et al<sup>(18)</sup> and Andrews et al<sup>(19)</sup> have reported the deposition of alumina and Krishnarao<sup>(20)</sup> has reported the deposition of magnesia in various organic media. Holzinger<sup>(21)</sup> used electrophoresis for electroplating of paint. Powers<sup>(14)</sup>, Kennedy et al<sup>(15)</sup>, Fally et al<sup>(6)</sup>, Baral<sup>(16)</sup>, and Krishnarao<sup>(17)</sup> have investigated the possibilities of using this technique for fabrication of thin walled  $\beta$ -alumina tubes. The important advantages of forming by electrophoresis are (a) high throwing power, (b) uniform thickness of the product, (c) short deposition time required, (d) versatility, so that a wide variety of shapes are possible and (e) relatively simple tooling.

### I.7.A Theory of Electrophoresis.

Electrophoresis is the movement of the suspended particles through a fluid under the action of an applied electric field. The particles carry electric charges which are acted by the field, thus producing motion through the fluid.

The charge of the particles may be either positive or negative. Positive particles migrate towards the cathode, and the phenomenon is then known as 'cataphoresis'. The migration of negative particles towards anode is known as 'anaphoresis'. The term electrophoresis is used to describe the general effect and the terms, cataphoresis and anaphoresis are being used to distinguish the sign of the charge and the direction of the migration. The charge on the particles and its magnitude are important for electrophoresis.

Three mechanisms for the generation of the charge have been proposed: (i) an unequal transfer of positive or negative ions from the surface of the solid to the liquid; (ii) a preferential adsorption of ions on the solid particles from the liquid medium; and (iii) an orientation of dipolar molecules present on the surface of the solid particle. These three mechanisms give rise to an electric double layer at the particle surface and to a potential difference across the phase boundary. Stern proposed a model in which the double layer is divided into two parts; the first part

consists of counterions attracted to the charged surface, and these ions are located in the 'stern layer' which has a thickness of about one solvent molecule. The second part is mobile and is called the diffuse layer. The potential difference between the solid surface and the stern layer is called the 'stern potential', while the potential difference between the stern layer and the bulk of solvent is called the 'Zeta potential'. If we assume that the double layer acts as an electric capacitor, the electrophoretic velocity,  $v$ , is given by

$$v = \frac{\xi \epsilon E}{4\pi\eta} \quad (I.1)$$

where  $\xi$  is the zeta potential,  $E$  is the potential gradient,  $\epsilon$  is the dielectric constant of the medium and  $\eta$  is the viscosity of the medium. When an electric field is applied, the solid particles move with their stern layer thus the electrokinetic studies are directly related to the zeta potential.

#### I.7.B Kinetics of Electrophoresis.

Hamaker<sup>(22)</sup> carried out many experiments under different conditions to obtain yield (in gms) as a function of deposition time and yield as a function of applied voltage. The details of the experimental conditions are given in Table I.3.



Table I.3

Characteristics of the suspensions used for  
electrodeposition by Hamakar<sup>(22)</sup>

No.	Depositing material	Vehicle	Concentration g/100 cc	Applied voltage Volts.	Deposition time sec.
1.	$\text{CaF}_2$	Ethanol	12	40	0-10
2.	$\text{BaSr}(\text{CO}_3)_2$	Ethanol + Methanol (1:1)	4.5	50	0-15
3.	$\text{Al}_2\text{O}_3$	Methanol	7.3	50	0-20
4.	$\text{BaCO}_3$	Methanol	6.2	20-200	3
5.	$\text{BaSrCO}_3$	Ethanol + Methanol (1:1)	1.8	20-250	5
6.	$\text{MgO}$	Methanol	3.2	20-250	3
7.	$\text{MgCO}_3$	Methanol	0.9	20-200	10

Combining the various results obtained, he proposed a straightforward law governing the electrophoretic yield. Yield was found to be proportional to time, surface, concentration and the applied electric field. Thus

$$y = a \int \mu F C A dt \quad (I.2)$$

where,  $y$  is yield in gms,  $\mu$  is the electrophoretic mobility ( $\text{cm}^2/\text{V sec}$ ), the velocity of the particle in a unit field of 1 V/cm;  $F$  is the electric field V/cm;  $C$  is the concentration of particles gm per cubic centimeter,  $A$  is the electrode area ( $\text{cm}^2$ ) and  $t$  is the deposition time (sec). 'a', takes account of the possibility that not all the particles which migrate to the electrode may deposit.

Avgustinik et al<sup>(18)</sup> deposited magnesia and glass in ethyl alcohol 96% and hydrochloric acid 1% medium; on thin (0.5 mm dia) copper wire for different times and voltages. For selection of optimum deposition conditions, a theoretical yield relationship was derived considering the geometry of the cell. Thus the equation proposed is

$$\gamma = \frac{U \zeta \epsilon c t l}{3 \ln \frac{r_1}{r_2} \eta} \quad (I.3)$$

where  $\gamma$  is the yield in gms,  $U$  is the voltage applied,  $\zeta$  is the zeta potential,  $\epsilon$  is the dielectric constant of the medium,  $t$  is the time,  $l$  is the length of the depositing electrode,  $\eta$  is the viscosity of the medium and

$r_1$  and  $r_2$  are the radii of inner and outer electrodes respectively.

The experimental results between the yield of deposit and the deposition time at constant voltage and between yield of deposit and voltage at constant deposition time agree with the theoretical yield calculated from equation (I.3) to a close approximation. The small deviations observed could be due to non uniform fall of potential during the deposition, which changes the field. As the deposit grows, dielectric becomes two layered (stern layer and diffused layer) and the field strength falls unequally in these layers, so that the potential gradient over the coated surface falls and yield of the deposit decreases.

Above 50 V, gas formation was observed and it is reported that it might be due to the electrolysis of HCl present in the suspension. Avgustinik et al have suggested that, equation (I.3) can be used for calculating the yield of the deposit for practical purposes, with a precision of about 15%.

Basically, equations (I.2) and (I.3) are same in all respects except that in equation (I.3) the dimensions of the cylindrical electrophoretic cell is considered. Equations are proved to be similar in the following way.

$$y = a \int \mu FCA dt \quad (I.2)$$

If we consider the cell as cylindrical, then the radial field

$$F = \frac{U}{\ln \frac{r_1}{r_2} \cdot r} \quad (I.4)$$

where  $r$ , is the radius, at the point where the potential gradient is to be determined and, from eq. (I.1),

$$\mu = \frac{v}{E} = \frac{\xi \epsilon}{6\pi\eta} \quad (I.5)$$

Substitution of eqs. (I.4) and (I.5) in eq. (I.2) gives

$$y = a \int \frac{\xi \epsilon U CA dt}{6\pi\eta \ln \frac{r_1}{r_2} \cdot r}$$

where  $r_1 = r$ , the potential gradient determined is at the mandrel surface and surface area of the mandrel =  $2\pi r l$ .

$$\begin{aligned} \therefore y &= a \int \frac{\xi \epsilon U C l dt}{3 \ln \frac{r_1}{r_2} \eta} \\ &= a \frac{U \xi \epsilon C l t}{3 \ln \frac{r_1}{r_2} \eta} \end{aligned} \quad (I.6)$$

Equation (I.3) or (I.6) is more accurate than equation (I.2) for theoretical calculation of yield, because, in equation (I.3) or (I.6) the radial field is considered which is present in a cylindrical cell (present case), whereas in

equation (I.2), only linear fields are considered, which is not the true field in a cylindrical cell.

#### I.7.C Electrophoretic Deposition as a Forming Technique.

Andrews et al<sup>(19)</sup> used electrophoresis as a forming technique. They investigated the feasibility of this process for the fabrication of thick, hollow alumina bodies of good surface finish, without the need of further machining. The depositions were carried using different liquids like ethanol, methyl-ethyl-ketone and mixture of toluene and ethanol. They suggested that ethanol suspension of 200 g alumina in 380 ml ethanol and 1 ml water with dewaxed shellac as binder gave good results for green bodies. The rate of deposition depends on concentration and applied voltage, and it decreased with continuous usage of the suspension and the variation of yield as a function of number of depositions was observed to be nonlinear. The releasing of the deposits gave problems. They could produce hollow alumina bodies using metallised plastic cocoons.

Fally et al<sup>(6)</sup> fabricated closed end tubes of  $\beta$ -alumina of thickness upto 600  $\mu\text{m}$  by this technique. The deposition was carried out in an organic liquid (no particular name of the liquid is mentioned), on metallic rods (cathode). The dried tubes were removed by isostatic pressing and sintered at about 1850°C in air with a propane-oxygen. The tubes thus obtained were used for Na/S cell

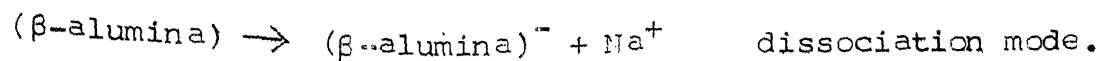
Kennedy et al<sup>(15)</sup> fabricated  $\beta$ -alumina tubes by depositing in dichloromethane medium (40 g  $\beta$ -alumina in 500 ml dichloromethane) on positive graphite electrodes. The tubes were obtained after burning the dried graphite rods at 800°C for 3 days. 3-4 cm long, 0.03-0.1 cm thick tubes were obtained and sintered at about 1700°C for 1.5-2 hrs. The velocity equation (equation I.1) was verified with respect to voltage (100-400 V) at a fixed depositing time (1 min) and with respect to deposition time (0-2 min) at a fixed voltage (200 V). The experimental yield rates are  $1.87 \times 10^{-3} \text{ g/cm}^2 \cdot \text{min} \cdot \text{V}$  and  $4.9 \times 10^{-3} \text{ g/cm}^2 \cdot \text{min} \cdot \text{V}$  respectively. The best results were obtained when 2 to 6 g of trichloroacetic acid was added to the suspension which helped in stabilizing the rapid flocculation and rapid settling. Presence of water gave flaky deposits and cracks were observed after drying. They have reported that presence of acid is a must for deposition.

Powers<sup>(14)</sup> used commercial  $\beta$ -alumina for fabrication of closed end tubes. The depositions were carried on stainless steel mandrels (anode) in n-amyl alcohol medium (100 g of  $\beta$ -alumina in 200 ml of n-amyl alcohol) for about 1 minute at 200-1000 V (corresponding to a field of 280 V/cm - 1400 V/cm). High voltage decreased the time of deposition to obtain the desired thickness, hence no stirring was required during the depositions. The

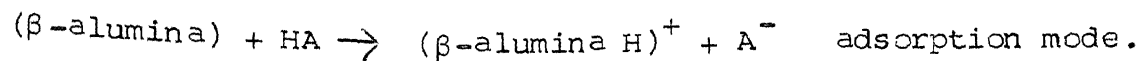
depositions were removed after complete elimination of liquid between the mandrel and the deposits. Some difficulties were encountered during this stage. The tubes thus obtained were sintered between 1700-1825°C and had sintered density in the range of 2.98-3.15 g/cm<sup>3</sup>.

Problems associated with electrophoretic forming have been discussed by Powers<sup>(14)</sup>. The selection of vehicle for the deposition is an important step. Not all organic solvents will give depositions, but only those organic liquids whose dielectric constant is in the range of 12-25 show the deposition behaviour. Use of low conductivity liquids is recommended with higher voltages and lower depositing time.

Two charging modes for  $\beta$ -alumina have been suggested; one is dissociation of sodium ions to give rise to a negatively charged particles. Thus



The second mode is the adsorption of protons or other cations which leads to positively charged particles. Thus



Proton donors might be water or organic acids.

The addition of water provides excess of protons and charge neutralization occurs in case of negatively

charged particles and excess of water gives positive charged particles (0.2-0.5% concentration). Higher amount of water (about 5%) leads to flocculation. Hence care must be taken to avoid moisture which affects the results. Powers used dry  $\beta$ -alumina powder and n-amyl alcohol, ground for long time ( $\approx$ 16-48 hrs) to get negatively charged particles. Longer grinding time gives finer particles but wear of the grinding media affects the quality of the deposits. Hence, an exceedingly hard and abrasive substance without incurring appreciable wear must be used. Water and wear of the grinding media which increases contamination will result in cracking of the dried deposits.

Another hurdle in the forming technique is releasing of the deposits. Many investigators have tried different methods. Powers reported that complete elimination of vehicle between mandrel and the deposits helps in easy removal. But in most of the cases, the deposits stick firmly to the mandrel which is difficult to release. Powers could get some tubes from negatively charged deposited particles and using slightly tapered mandrels. But, once again the ease of removal depends on starting materials. So, the desired properties of the starting material must be fine powder and negatively charged particles to get good deposits and hence the tubes.



Baral<sup>(16)</sup> investigated the possibilities of using different vehicles like acetone, isoamyl alcohol, dichloromethane and benzyl alcohol for electrophoretic deposition of  $\beta$ -alumina. First, qualitative experiments were carried out with 100 g of  $\beta$ -alumina and 200 ml of vehicle, ground for 2-4 hrs and deposited on stainless steel mandrels. Using a 250 ml glass beaker as container, a perforated stainless steel tube as counter electrode, and tapered stainless steel mandrels as depositing electrodes. The beaker was rotated for about 1 min just before the depositions were done, to prevent settling. Acetone did not give any deposition while dichloromethane gave deposition on positive electrode. But it was difficult to get stable suspension with these vehicles. Iso-amyl alcohol and benzyl alcohol gave stable suspensions and depositions were obtained. In case of benzyl alcohol drying was rather slow, because of its higher boiling point. Good depositions were obtained in iso-amyl alcohol medium with few cracks after drying. It was not possible to remove tubes intact from the mandrels. Further experiments were done using iso-amyl alcohol (200 ml) and 100 g of  $\beta$ -alumina and the yield (g) was obtained as a function of deposition time (1.5-4 min at 200 v) and applied voltage of 100-300 v with U.S. amyl alcohol and 200 to 400 v with industrial amyl alcohol. The results show only three points with two different slopes. If we assume that

the deposited area is maintained same in all the cases, then the results deviate from the law. If we assume, that the areas varied, hence the deviation from the law then the correction cannot be made, due to the nonavailability of data (area). The similar behaviour is obtained with variation of time. Again only three points are shown, with two different slopes, area is not mentioned, hence difficult to judge whether the law is verified or not.

Krishnarao<sup>(17)</sup> evaluated a number of vehicles (dichloromethane, benzyl alcohol and five different varieties of amyl alcohol) for their suitability as the suspension medium for electrophoretic depositions of  $\beta$ -alumina. Among the vehicles evaluated, iso-amyl alcohol (BDH) was found to give satisfactory results because of its low conductivity, the use of higher voltages was possible. Additives like ethylene glycol and trichloro acetic acid were also tried to get good crack-free deposits, but porous depositions were obtained in these cases at higher voltages.

The depositions were carried out using a stainless steel (2.85 cm dia) can as container and counter electrode, and stainless steel mandrels. Yield ( $\text{g}/\text{cm}^2$ ) was obtained with respect to concentration, voltage and deposition time. About 40 g of  $\beta$ -alumina in 50 ml of vehicle was used for deposition. Voltage was varied from 0-500 V for 1 min depositions and time from 0-4 minutes, at an applied

voltage of 25 v. Verification of the kinetic equations (I.2) and (I.3) was not done fully due to difficulties in getting reproducible results. The vehicle was used as received without further purification. The nonreproducibility could be because of moisture adsorption by powder, vehicle and suspension at different stages of the experiments. The moisture affects the charge and conductivity of the suspension and thus leads to varying of the results.

As seen in earlier sections, still there are some problems to be solved in this area of electrophoretic deposition techniques. The existing problems are:

- (1) Verification of the proposed kinetic equations with reproducible results is not fully achieved.
- (2) It is reported that releasing of the deposits from the metallic mandrels is difficult.
- (3) Tubes were obtained (Kennedy et al<sup>(15)</sup>) after burning the deposited graphite mandrels. In this case, to get one tube, one graphite mandrel is required to be burnt, which is not attractive. Moreover, burning of coated graphite mandrel and getting crack-free tubes also has some problems.

## I.8 Present Work.

Keeping in mind the above problems to be solved the present study is designed to be carried out in the following steps:

- (1) As it is reported that varying amount of moisture affects the results, it is proposed to overcome this problem by using dry powder and dry, distilled amyl alcohol, to get reproducible results so that the kinetic equations may be verified, using voltage, time, concentration and electrode separation as the parameters.
- (2) Powers has reported that he could release the deposits by depositing negatively charged particles on tapered stainless steel mandrels and eliminating completely the vehicle between mandrels and the deposit. The earlier studies in this laboratory showed that only positively charged particles were deposited. Hence, an attempt is made here to obtain negatively charged particles and to deposit on tapered stainless steel mandrels and finally to release the deposits.
- (3) Burning of one graphite mandrel to get one tube is not economic and also there exists many problems during burning. So, the depositions on different types of mandrels have been tried, viz., (a) deposition of positively charged particles on tapered stainless steel mandrels, (b) deposition of negatively charged particles on tapered stainless steel mandrels, (c) deposition on graphite coated alumina rods and (d) deposition over tapered stainless steel mandrels which

are coated by wax and then by graphite. Hence, an attempt is made to obtain the tubes without damage using the above depositions on different types of mandrels.

## CHAPTER II

## EXPERIMENTAL PROCEDURES

The fabrication of  $\beta - \beta''$  - alumina in the form of closed end tubes by electrophoretic deposition consists mainly of four steps, viz.,

- (1) Preparation of  $\beta - \beta''$  - alumina,
- (2) Preparation of suspension,
- (3) Electrophoretic deposition, and
- (4) Removal of deposits,

## II.1 Preparation of $\beta - \beta''$ - Alumina.

### II.1.A Preparation of Mixture.

In the preparation of  $\beta - \beta''$  alumina,  $\text{Na}_2\text{O}$  loss occurs during high temperature calcination. But the  $\beta - \beta''$  alumina boundary starts from 1 : 5.33 ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$ ) ratio. So, to attain this ratio (1 : 5.33) excess soda is taken (1 : 5) in the beginning, and during calcination, the soda loss shifts the ratio to the range of 1 : 5.33 to 1 : 8.5. Hence the material is taken in the ratio of 1 : 5 in the present study. The starting materials used for making  $\beta''$  alumina ( $\text{Na}_2\text{O} \cdot 5 \text{Al}_2\text{O}_3$ ) were  $\beta$ -alumina (Alcoa-2) and sodium carbonate (BDH, Analar 99.9%).  $\alpha$ -alumina, heated to 800°C for 2-3 hours, as well as sodium carbonate were

preserved in an oven at a temperature of about 150-160°C to avoid the adsorption of moisture. The weight percentage required for  $\text{Na}_2\text{O} \cdot 5 \text{Al}_2\text{O}_3$  were calculated (as shown in Appendix A).

The mixture was prepared in batches each to yield 100 g of  $\beta - \beta''$  - alumina. The corresponding materials (89.16 g of  $\text{Al}_2\text{O}_3$  and 18.54 g  $\text{Na}_2\text{CO}_3$ ) were weighed accurately in a single pan balance (Mettler) to an accuracy of 0.1 g, and were mixed thoroughly under acetone (A.R.) medium, in a jar mill (porcelain) for about 2 hours. About 1100 g of sintered  $\alpha$ -alumina balls were used as grinding aid. The milled mixture was transferred to a beaker and allowed to dry at room temperature, and finally oven dried. Similarly, other batches were prepared and kept ready for calcination.

#### II.1.B Calcination.

The oven dried mixture of  $\beta\text{-Al}_2\text{O}_3$  and  $\text{Na}_2\text{CO}_3$  was transferred to platinum crucibles, in the form of lumps. The platinum crucibles filled with dried mixture were kept inside a globar furnace with the lids closed, and temperature was raised slowly from about 500°C to 1225°C. After calcination for 4-4.5 hours, the temperature of the furnace was reduced to 800°C in steps. Then the crucibles were removed from the furnace, cooled to room temperature, and the calcined material was transferred to a clean dry beaker and stored in an oven at 150-160°C till further use.

### II.1.C Characterization of Calcined Powder.

The presence of  $\beta$  and  $\beta''$  alumina phases in the calcined powder was characterized using X-ray diffractometer (General Electric, XRD-5). The calcined powder was crushed to powder in an automatic pestle and mortar (The Torsion Balance Company) for half an hour. A small amount (about 1 g) of the powder was used for X-ray study in a plexiglass specimen holder.  $\text{CuK}_\alpha$  radiation with Ni filter (at 500 cps, scanning rate  $2^\circ/\text{min}$  and chart speed  $1''/\text{min}$ ) was used for X-ray diffraction. The powders was scanned from  $7^\circ$  to  $70^\circ 2\theta$ . The 'd' values obtained from the experiment, were compared with standard 'd' values from ASTM file. The calcined powder was found to consist of only  $\beta$  and  $\beta''$  alumina with traces of sodium aluminate.

To determine the approximate relative amounts of  $\beta$  and  $\beta''$  alumina and thereby the degree of conversion after calcination, a normalised index (Ref. 23)  $f(\beta) = \frac{I(\beta)}{I(\beta) + I(\beta'')}$  was calculated using the integrated intensities of  $\beta$  and  $\beta''$  alumina at  $2\theta = 44.3^\circ$  and  $46^\circ$  respectively.

The powder density of the calcined powder was measured using a specific gravity bottle and toluene (liquid) at room temperature.



## II.2 Suspension Preparation.

$\beta$  -  $\beta''$  - alumina suspensions for the experiments were prepared by grinding a known amount of dry powder and a known volume of distilled <sup>iso</sup>/amyl alcohol (BDH A.R.) in a porcelain jar with sintered alumina balls as the grinding aid. The previous<sup>(16, 17)</sup> studies done in this laboratory showed that a fairly good amount of depositions with good surface finish were obtained with 50-60 g of  $\beta$ -alumina powder in 100 ml of iso-amyl alcohol at 400-500 v applied, for 1 minute. With increase in grinding time, yield was observed to increase, but increment in yield was more drastic in the first 1½ hours, compared to further 7 hours of grinding. Hence, on this basis, it was decided to use a suspension of 60 g of powder in 100 ml of distilled iso-amyl alcohol medium, ground for 5 hours in most of the experiments described here.

The alcohol was distilled by fractional distillation column just before using it for the experiments. The fraction used was collected in its boiling range 128-131°C. In most of the cases 120 g of  $\beta$  -  $\beta''$  alumina (taken from the oven, cooled to room temperature) was ground for 5 hours in 200 ml of distilled iso-amyl alcohol medium. Care was taken not to expose the suspension to atmosphere as far as possible. The suspension thus prepared was used for different experiments.

## II.3 Electrophoretic Deposition.

### II.3.A Electrophoretic cell.

The electrophoretic cell used for the experiment is shown in Figure II.1. It is similar to the one used by earlier investigators<sup>(17, 20)</sup>. This consists of depositing mandrels and a closed end stainless steel can used as container and the counter electrode. The mandrels used for deposition were made of different materials viz., tapered stainless steel (which have been used by Krishnarao<sup>(17)</sup>), wax coated stainless steel, graphite and graphite coated alumina rods. The stainless steel mandrels were coated with molten wax, and a thin graphite (graphite in water) coating was given over the wax surface, thus making the surface conducting. The alumina rods were also coated with graphite by using graphite paint in linseed oil medium. All the mandrels used were tapered.

The electrical circuit used for electrophoretic deposition is shown in Figure II.2. Aplab D.C. Power Supply (0-500 V and 0-500 mA) was used as the source for the deposition. The electrodes were connected with proper polarity depending on the charge of the particles, so as to get the deposit on the mandrels. For studying the effect of electrode separation, counter electrodes of different diameters (1.85, 2.85 and 3.45 cm) were used.

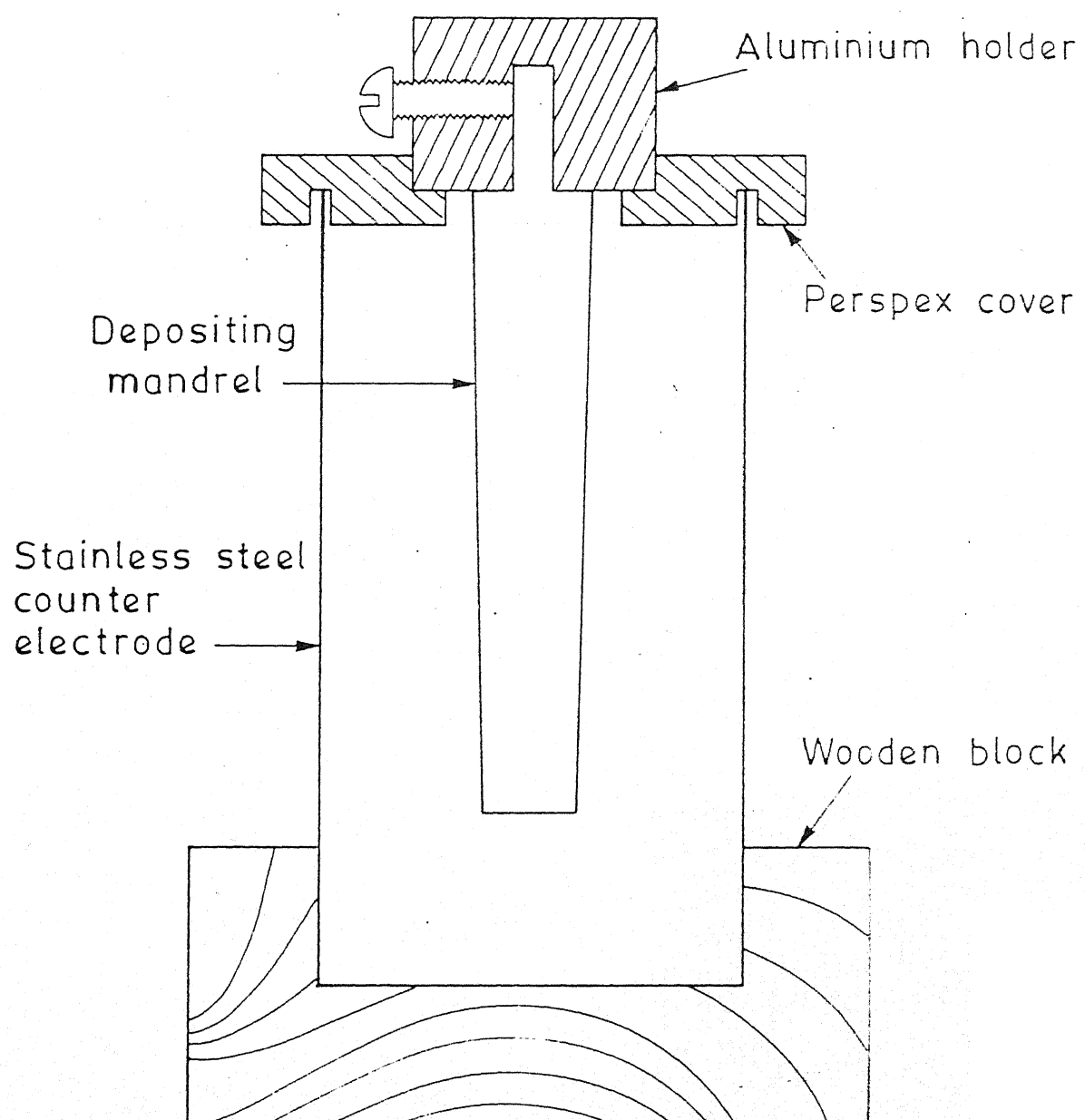


Fig. II.1 Electrophoretic cell.

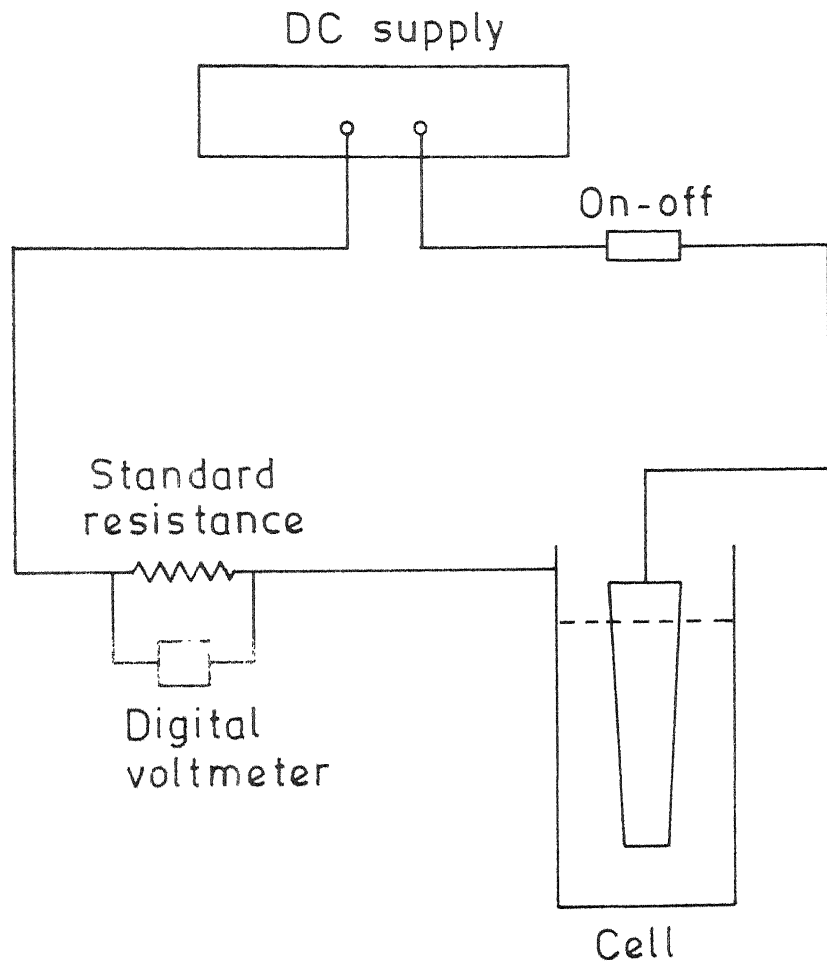


Fig. II.2 Electric circuit.

During the depositions, the current was measured by a digital voltmeter (Yamuna) as the voltage across a standard resistance.

### II.3.B Deposition.

The electrophoretic depositions of  $\beta - \beta''$  - alumina were carried out on different tapered mandrels. Only stainless steel mandrels were used for making kinetic study and other mandrels (stainless steel mandrels coated with wax and graphite, and graphite coated alumina rods) were tried to facilitate the removal of the deposits.

To study the effect of concentration of the suspension on the deposition rate, a number of depositions were carried out one after the other from the same suspension. The suspension was stirred thoroughly with a glass rod before each deposition. All the depositions were carried out at 450 v for 1 minute. 60 g of  $\beta - \beta''$  alumina and 100 ml distilled<sup>iso</sup>/amyl alcohol were used to prepare the suspension. In this case, the concentration decreased because of successive depositions. The dried deposits were weighed and the yield was calculated as  $\text{g/cm}^2$ . The concentration ( $\text{g}/100 \text{ ml}$  of suspension) was calculated by knowing the weight of the powder and the volume of the suspension at the beginning of each deposition. A sample calculation for finding out the concentration is shown in Appendix B.

In order to study the effect of voltage on the deposition yield, the depositions were carried out at different voltages in the range of 100-500 v for 1 minute on stainless steel mandrels. For this purpose, 120 g of  $\beta - \beta''$  alumina and 200 ml distilled <sup>iso</sup>/amyl alcohol were used for making the suspension in bulk. From this bulk suspension, a fresh supply of about 35 ml was used for each deposition and the suspension remaining after each deposition was discarded. In this way, maintaining the concentration almost same, different depositions were carried out in the range of 100-500 v.

Similarly, maintaining the concentration 100 g  $\beta - \beta''$  alumina in 200 ml distilled isoamyl alcohol of the suspension and the applied voltage (500 v) constant, depositions were carried out for different time periods (10-50 seconds) on stainless steel mandrels, to obtain yield as a function of deposition time.

The effect of electrode separation on yield was studied by changing the gap between the two electrodes. This was done by using counter electrodes of different diameter (1.85, 2.85 and 3.45 cm). Concentration was maintained almost the same for these three sets of depositions also, in a similar way as mentioned above. All the depositions were carried out at 500 v for 1 minute. The yield  $\text{g/cm}^2$  was calculated by knowing the weight of the deposit and the deposited area.

Attempts were made to remove the deposits without any damage after depositing on different electrodes viz., wax coated stainless steel, graphite and graphite coated alumina rods. A thick wax coating can be easily removed in the form of a hollow tube. So, the wax coating on stainless steel mandrel, was made conducting by painting graphite (graphite paint in water) with a paint brush. Tapered alumina rods were made by slip casting and were sintered. These rods were coated with graphite, using graphite paint made in commercial linseed oil medium. After the deposition of  $\beta$  ..  $\beta$ " alumina over these mandrels, they were dried at room temperature. No quantitative yield study was made with these depositions, since these experiments were designed to examine the relative ease with which deposits could be removed from the mandrels.

#### II.4 Removal of Deposits.

Several methods were tried to remove the dried deposits in order to get closed end tubes without any damage. Hand pulling, quenching in acetone and liquid nitrogen medium, burning the graphite layer from the alumina rods and removing directly with wax are the methods tried.

The dried deposits from the stainless steel mandrels were hand pulled after cutting the starting end with a blade. Due to the unequal pressure during pulling,

it was found difficult to get crack-free tubes. Quenching in acetone and liquid nitrogen were done, thinking that, at low temperature, the mandrel shrinks and facilitates the easy removal. This was done by slow immersion of the mandrel in liquid medium used and holding there for a few minutes. This also did not give any encouraging results. The deposited graphite coated alumina rods were heated in furnace slowly upto  $600^{\circ}\text{C}$  and cooled slowly so as to burn off the graphite layer present in between the deposit and the alumina rods. The deposits of wax coated stainless steel mandrels were removed by just pulling the whole deposit along with the wax skeleton. The removal of wax coated deposit was very easy and very little pressure was required.



## CHAPTER III

## RESULTS AND DISCUSSIONS

## III.1 Characterization of Calcined Powder.

## III.1.A Phase Analysis.

The presence of  $\beta$ - and  $\beta''$ -alumina phases in calcined powder was detected by X-ray diffraction. The  $2\theta$  and  $d$  values obtained for the samples were compared with standard X-ray patterns. For a semi-quantitative estimation of the two phases, a normalised index suggested by Youngblood et.al.<sup>(23)</sup>.  $f(\beta) = \frac{I(\beta)}{I(\beta) + I(\beta'')}$ , where  $I(\beta)$  and  $I(\beta'')$  are the integrated intensities corresponding to  $\beta$  and  $\beta''$  alumina respectively was used. The samples were scanned at slow rate ( $0.4^\circ$  per minute) in the range of  $2\theta = 40^\circ$  to  $48^\circ$ , so as to get well separated peaks of  $\beta$ - and  $\beta''$ -alumina at  $2\theta = 44.3^\circ$  and  $2\theta = 46^\circ$ , respectively. The  $f(\beta)$  found for different sets of calcined powder is shown in Table III.1.  $f(\beta)$  varied from 0.19 to 0.39. This variation could be because of some unintended difference in calcining conditions viz., heating rate, holding time, temperature of calcination etc. as well as the errors in X-ray intensity measurements. The  $f(\beta)$  is proportional to the amount of  $\beta$  phase and the balance consists of  $\beta''$  phase, along with traces of sodium aluminate (upto 4%).

Table III.1

Amount of  $f(\beta)$  in calcined powder

Sample No.	Amount of $f(\beta)$
1	0.23
2	0.19
3	0.28
4	0.30
5	0.25
6	0.32
7	0.36
8	0.39

The presence of sodium aluminate was estimated by treating the two calcined samples with hot, distilled water in HCl medium. The sodium aluminate content found was about 7-9%. In these cases, the crucibles were kept inside the furnace at about 1050°C and after calcining at 1050°C for about 4 hours, the crucibles were taken out of the furnace. The larger sodium aluminate content observed could be because of insufficient calcination temperature and time. This difficulty was overcome in later cases by starting the calcination from low temperature (about 500°C) then increasing it slowly upto 1250°C and decreasing slowly down to 800°C after calcining for 4-5 hours. Sodium aluminate content in such samples was not more than 4%. During the calcination, two things happen, viz. evolution of CO<sub>2</sub> around 850°C and solid state reaction to form  $\beta$  and  $\beta''$  alumina phases. Elimination of CO<sub>2</sub> should be complete before the solid state reaction. The complete evolution of CO<sub>2</sub> was confirmed by making weight loss measurements. Theoretically, the calcined material should lose about 7.2% weight (Appendix C). If the weight loss is less than the expected value, then calcination is not complete. In the present study, the weight loss observed was in the range of 7.18 to 7.26%, which showed complete elimination of CO<sub>2</sub> during the process of calcination.

### III.1.B Density of the Calcined Powder.

The density of calcined powder was found to be 3.23 g/cc when measured in toluene medium using a specific gravity bottle. The observed value is close to the theoretical density reported 3.27 g/cc<sup>(24)</sup>.

### III.2 Factors Governing the Electrophoretic Depositions.

#### III.2.A Moisture.

Moisture affects the electrophoretic depositions to a great extent, if it is not controlled to within some limits. The powder, alcohol, and suspension adsorb moisture at different stages of the experiment in varying proportions and hence give non-reproducible results. To get reproducible results, all parameters must be maintained constant and it is necessary to use dry powder and dry distilled alcohol. Figure III.1 show the results obtained using distilled and non-distilled alcohols. Here yield ( $\text{g/cm}^2$ ) is plotted as a function of concentration of the suspension ( $\text{g/100 ml}$  of suspension), keeping duration of the deposition fixed at 1 minute and the applied voltage at 450 V. Curves B, C and D are obtained using non-distilled alcohol keeping all other parameters the same. Similarly curves E and F were obtained using dry  $\beta$  -  $\beta''$  alumina and distilled iso amyl alcohol while maintaining other parameters constant. The variation in results between the two

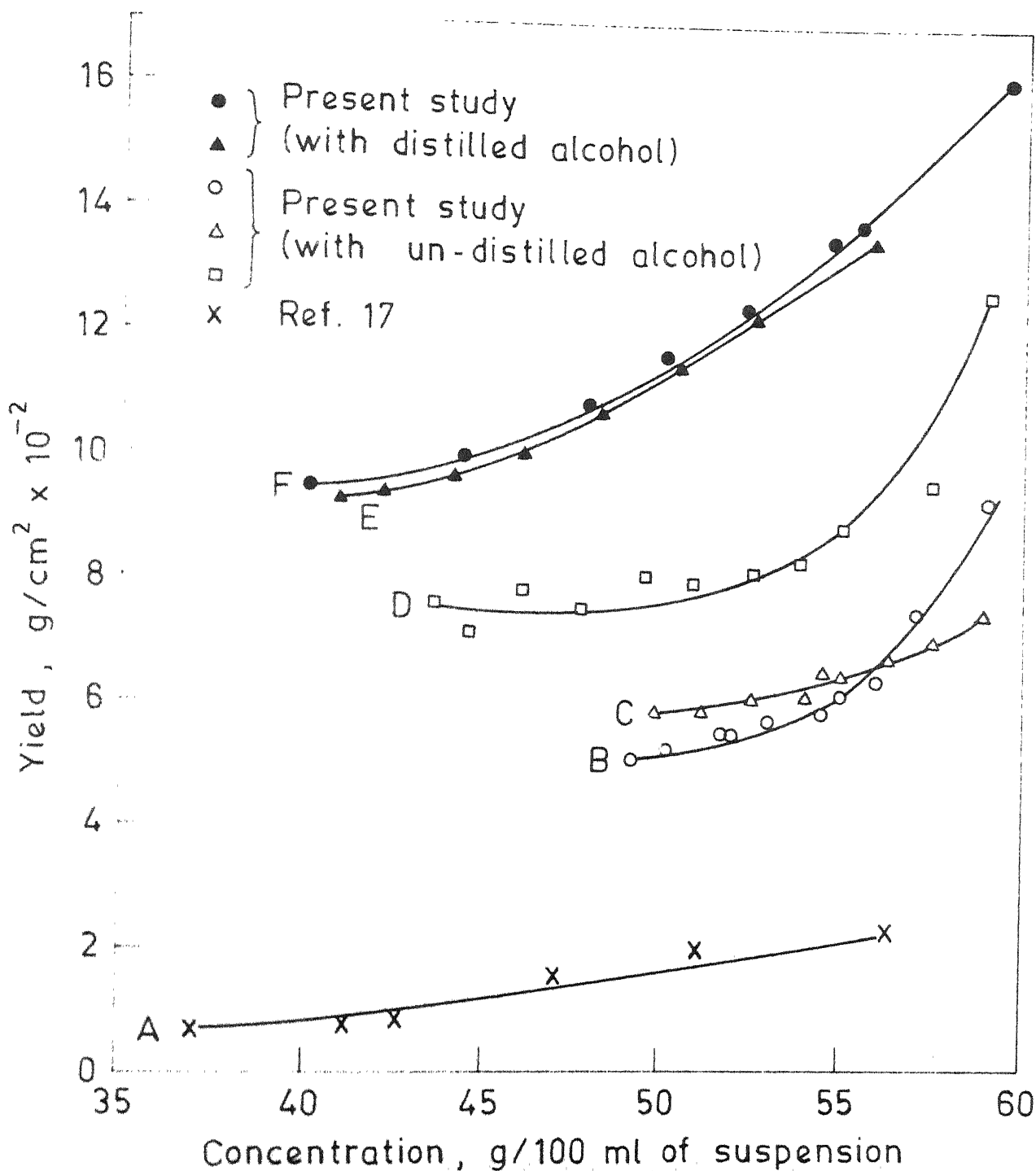


Fig. III. 1 Variation of yield with concentration of  $\beta$ - $\beta''$  alumina suspension at 450 V, for 1 minute deposition.

sets (viz. with distilled and nondistilled alcohol) is substantial. Also seen is a large scatter in the yield data when the amount of moisture is not controlled, leading to non-reproducible results. On the other hand, the two sets of yield data obtained with distilled iso-amyl alcohol exhibit good reproducibility. Hence, to get reproducible results, it is necessary to maintain all the parameters the same and even moisture must be controlled.

Powers<sup>(14)</sup> has reported the effects of water on electrophoretic depositions. Addition of water gives rise to protons and hence increases positive charge. If the initial charge of the particles is negative, then the moisture affects a charge inversion and finally neutralization. Kennedy et.al.<sup>(15)</sup> observed this charge inversion in dichloromethane suspension. With excessively dry powder and dry alcohol, the deposited materials slips down from the mandrel. Hence there is a limit for moisture to be present for good electrophoretic depositions. The charge inversion and neutralisation was observed with 0.2 to 0.5% of moisture in  $\beta$ -alumina/n-amyl alcohol suspension. It is reported that with still larger amount of water (about 5%) charge neutralisation takes place a second time giving no deposition. The deposits with large water content give flaky, weak deposits and dried deposits give cracks. Kennedy et al<sup>(27)</sup> have reported the variation of

mobility of  $\beta$ -alumina in pentanol with water content. Mobility remains constant for water content of 0.1 to 2 g/l, increases from 2-20 g/l and decreases from 20-50 g/l. At contents more than 50 g/l flocculation occurs and the suspension settles down very fast. Kennedy et al<sup>(15)</sup> got flaky, poorly adhered deposits of  $\beta$ -alumina in a suspension of 40 g  $\beta$ -alumina, 6 g trichloroacetic acid, 500 ml dichloromethane and 1 ml of water. The water also leaches the  $\text{Na}^+$  from  $\beta$ -alumina and hence decreases the zeta potential. Hence, to get good electrophoretic depositions, it is required to control the moisture content and the little amount of moisture which is essential for deposition can be achieved during the experiment<sup>(14)</sup>. The charging of  $\beta$ -alumina is kinetically slow hence requires long grinding procedures. Powers used long grinding time to get negatively charged particles of  $\beta$ -alumina in n-amyl alcohol medium. The powder showed positive charges when put in n-amyl alcohol, because of addition of moisture from the atmosphere. During milling this was first neutralised and subsequently a negative charge developed after 2-8 hours, due to dissociation mode of charging. But a limitation of the dissociative mode of charging is that  $\beta$ -alumina particles must not be removed from the suspension before deposition after milling, otherwise a positive charge is acquired which then is most difficult to neutralise by further milling. This formation

of positive charge starting from negatively charged particles when they are exposed to atmosphere, is mainly due to adsorption of moisture<sup>(14)</sup>. Kennedy et al<sup>(27)</sup> reported that the best electrophoretic deposits occurred when zeta potential had a low absolute value. So to get good reproducible results, it is necessary to control the moisture.

### III.2.B Concentration.

The effect of concentration on yield was studied by varying the concentration and carrying out successive depositions at 450 v for 1 minute. The concentration varied from 60 g/100 ml of suspension to 40 g/100 ml of suspension. The yield ( $\text{g/cm}^2$ ) is plotted as a function of concentration (Figure III.1). A variation in yield is observed  $16 \times 10^{-2} \text{ g/cm}^2$  ( $3.56 \times 10^{-4} \text{ g/cm}^2 \cdot \text{min.v}$ ) at 60 g/100 ml of suspension to  $9 \times 10^{-2} \text{ g/cm}^2$  ( $2 \times 10^{-4} \text{ g/cm}^2 \cdot \text{min.v}$ ) at 40 g/100 ml with decrease in concentration. The results may be compared with those of Powers<sup>(14)</sup> and Krishnarao<sup>(17)</sup>. Starting with a concentration of 100 g of  $\beta$ -alumina in 200 ml of n-amyl alcohol, Powers<sup>(14)</sup> carried out a number of depositions and deposition time was adjusted such that almost the same amount of material was deposited every time. This process was continued till about 80% of the solids were removed. The yield (g/min) was found to decrease when plotted as a function deposition numbers,



the decrease being slightly nonlinear. With the available data it is not possible to express these results in terms of concentration and yield ( $\text{g}/\text{cm}^2$ ). Krishnarao<sup>(17)</sup> varied concentration by adding the iso-amyl alcohol to the suspension range from 76 to 36 g of  $\beta$ -alumina/100 ml of suspension. The depositions were carried out at 100 v for 1 minute duration. The yield rate ( $\text{g}/\text{cm}^2 \cdot \text{min} \cdot \text{V}$ ) variation is from  $5 \times 10^{-4} \text{ g}/\text{cm}^2 \cdot \text{min} \cdot \text{V}$  at 76 g/100 ml to  $1 \times 10^{-4} \text{ g}/\text{cm}^2 \cdot \text{min} \cdot \text{V}$  at 36 g/100 ml. The curve is incorporated in Figure III.1. A nonlinear behaviour of yield as a function of concentration was observed by him also. In the concentration range where Krishnarao as well as the present study obtained yield data, the yields of Krishnarao are always significantly lower than those of the present work at the same concentration. This may be attributed to the presence of moisture in the suspension used by Krishnarao, since he did not distill alcohol. This contention of moisture lowering the yield is substantial by lower yield results obtained with undistilled alcohol compared to those obtained with distilled alcohol in the present study also (Figure III.1).

According to equations (I.2) and (I.3) the yield behaviour should be linear when plotted against concentration. The nonlinear behaviour could be because of the following reasons:

- i) all the particles reaching the mandrel may not be depositing, and

- ii) the probability that the particles moving more rapidly drag slower particles with them, particularly at the higher concentrations, thus raising the specific yield<sup>(18)</sup>.

### III.2.C Voltage.

The effect of voltage on yield is studied by carrying out the depositions in the range of 50 to 500 v for 1 minute, maintaining other parameters almost same as explained in section II.3.B. Experiments were done at the intervals of 100 v, starting from 50 v and 100 v in two separate experiments. The yield ( $\text{g}/\text{cm}^2$ ) is plotted as a function of applied voltage (Figure III.2). As expected from equations (I.2) and (I.3) a linear behaviour is observed. The curves showed zero intercept at zero applied voltage, which indicates that at zero field no deposition takes place. The slope of yield versus voltage curve is  $5 \times 10^{-4} \text{ g}/\text{cm}^2 \cdot \text{min} \cdot \text{V}$ .

The present results can be compared with the results of Krishnarao<sup>(17)</sup> for  $\beta$ -alumina in iso-amyl alcohol medium and Kennedy et al<sup>(15)</sup> for  $\beta$ -alumina in dichloromethane. Krishnarao has reported the variation of yield ( $\text{g}/\text{cm}^2$ ) with applied voltage for different grinding times with one minute depositions. 100 g of  $\beta$ -alumina in 200 ml of iso-amyl alcohol was used and ground for 0, 1.5 and

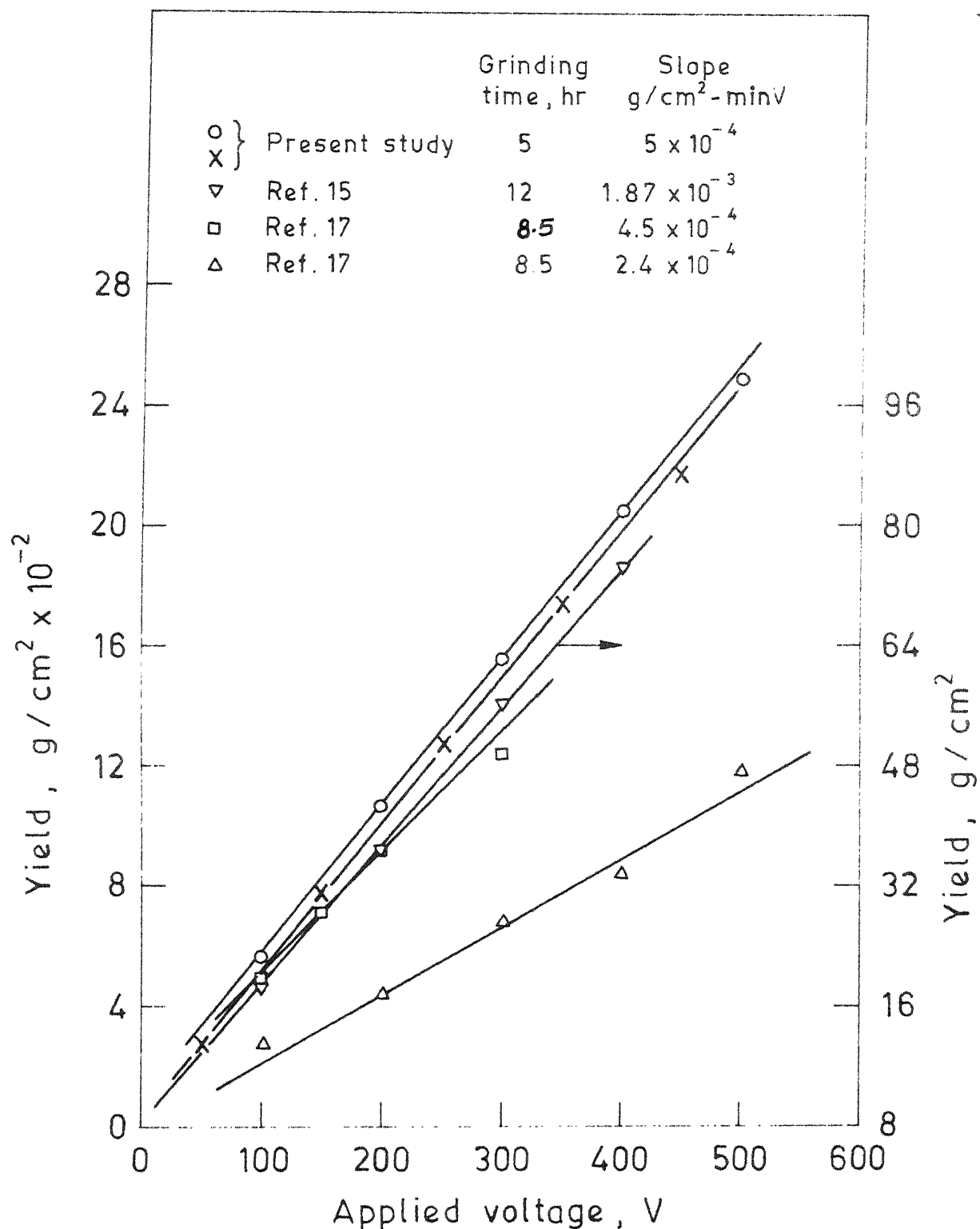


Fig. III. 2 Variation of yield as a function of applied voltage for 1 minute. 120 g  $\beta$ - $\beta''$  alumina in 200 ml iso-amyl alcohol.

8.5 hours, the slopes corresponding to these depositions are  $2.4 \times 10^{-4}$ ,  $3.7 \times 10^{-4}$  and  $4.5 \times 10^{-4}$  g/cm<sup>2</sup>.min.v respectively. Curves corresponding to 0 and 8.5 hours are shown in Figure III.2. The slope of 8.5 hours grinding is comparable to that in the present study ( $5 \times 10^{-4}$  g/cm<sup>2</sup>.min.v), where only 5 hours of grinding time was employed. Though straight line relation is observed for these three curves, they have different intercepts viz. 0,  $1 \times 10^{-2}$  and  $2 \times 10^{-2}$  g/cm<sup>2</sup> respectively with 0, 1.5 and 8.5 hours of grinding. The intercepts of  $1 \times 10^{-2}$  and  $2 \times 10^{-2}$  g/cm<sup>2</sup> suggest sticking of the suspension to the mandrel even at zero field. The suspension which is not ground gives zero intercept.

Kennedy et al<sup>(15)</sup> got a slope equal to  $1.83 \times 10^{-3}$  g/cm<sup>2</sup>.min.v with 40 g of  $\beta$ -alumina and 4 g of trichloroacetic acid in 500 ml of dichloromethane deposited for 1 minute. This value is 3 to 4 times that of the present study. These results are also included in Figure III.2 which shows a linear dependence passing through the origin hence in agreement with equations (I.2) and (I.3). The higher slope of Kennedy et al could be due to the fact that a different vehicle viz. dichloromethane was used in his work compared to isoamyl alcohol used in the present work as well as by Krishnarao<sup>(17)</sup>. Secondly an acid was added while no such addition was made in the present work. Baral<sup>(16)</sup> has

### III.2.D Time.

The effect of depositing time on yield is studied by carrying out the depositions in the range of 10 to 50 seconds at 500 v with suspension containing 50 g  $\beta$  -  $\beta''$ -alumina in 100 ml of distilled iso amyl alcohol maintaining other parameters almost the same as explained in Section II.3.B. The yield ( $\text{g/cm}^2$ ) is plotted as a function of deposition time in Figure III.3 for two experiments carried out separately. The two sets of results show a linear dependance of yield as deposition time, passing through origin, in agreement with equations (I.2) and (I.3). The slopes of two lines are  $3.6 \times 10^{-4}$  and  $3.9 \times 10^{-4}$   $\text{g/cm}^2 \cdot \text{min.v}$ . Within the limits of error of present experiment these two slopes may be considered to be same.

Krishnarao<sup>(17)</sup> has reported the yield ( $\text{g/cm}^2$ ) as a function of deposition time (0 to 4 minutes) at 25 v for different grinding times, viz., 0, 1.5 and 8.5 hours, the slopes corresponding to these are  $2.4 \times 10^{-4}$ ,  $6.4 \times 10^{-4}$  and  $8.8 \times 10^{-4}$   $\text{g/cm}^2 \cdot \text{min.v}$ . One of his results is included in Figure III.3, which shows a linear dependance with a slope of  $8.8 \times 10^{-4}$   $\text{g/cm}^2 \cdot \text{min.v}$  for suspensions ball milled for 8.5 hours. The higher yield rate obtained by Krishnarao compared to that of the present study may be due to the larger grinding time employed in former. This must have resulted in a finer particle size of Krishnarao's material

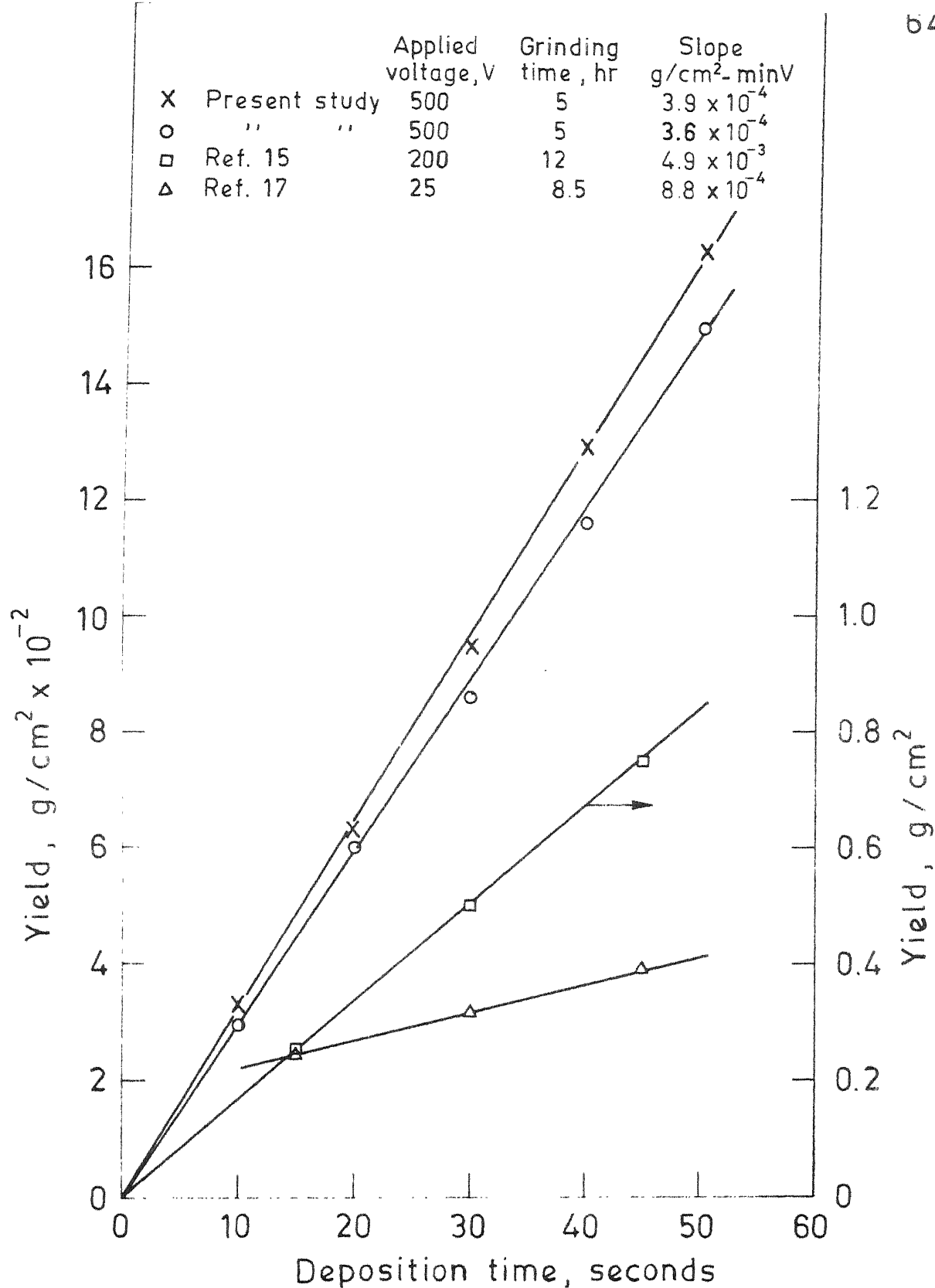


Fig. III.3 Variation of yield as a function of deposition time at 500 V. 100 g  $\beta$ - $\beta''$  alumina in 200 ml iso-amyl alcohol.

than that in the present work and this is corroborated by the fact that a positive intercept of nearly  $2 \times 10^{-2} \text{ g/cm}^2$  is observed by him, which is indicative of deposition taking place on the mandrel even in the absence of any applied field.

Kennedy et al<sup>(15)</sup> reported the yield ( $\text{g/cm}^2$ ) using 40 g of  $\beta$ -alumina, 6 g trichloroacetic acid in 500 ml dichloromethane suspension at an applied voltage of 200 v depositing at various deposition timings (0-2 minutes). The curve corresponding to this experiment is also included in Figure III.3 which shows a linear dependence passing through origin, in accordance with equations (I.2) and (I.3). However the yield rate of  $4.9 \times 10^{-3} \text{ g/cm}^2 \cdot \text{min} \cdot \text{V}$  observed is more than an order of magnitude higher than that obtained in the present work. Once again this large difference could be due to the fact that a different vehicle (dichloromethane) and 6 g of trichloroacetic acid was used in his work compared to isoamyl alcohol used in the present study. As stated in an earlier Section III.2.C the effect of addition of trichloroacetic acid gives higher yield. So, in his case use of 6 g of trichloroacetic acid gives much higher yield.

During each deposition decrease in current was observed with deposition time. This decrease in current is due to increase in resistance at the depositing electrode

surface, which decreases the potential drop across the suspension hence decreases the mobility. It has been demonstrated by several investigators (Berry<sup>(25)</sup> and Tasker et al<sup>(26)</sup>) that the weight of the deposit formed is approximately proportional to the number of coulombs of electricity passed during the the deposition, i.e. proportional to the integral of the current with respect to time. Depositions were carried out at two different concentrations, 50 g/100 ml and 60 g/100 ml of  $\beta - \beta''$  alumina in iso amyl alcohol medium at a 500 v for different deposition timings. The decrease in current during deposition was plotted as current density against deposition time. The area under the curve for each depositions is calculated which gives the quantity of electricity per unit area ( $Q/\text{cm}^2$ ). Thus the yield ( $\text{g}/\text{cm}^2$ ) is plotted against  $Q/\text{cm}^2$  (Figure III.4) for both the concentrations. These two curves obey the linear law with zero intercept, hence proving yield proportional to the quantity of electricity per unit area.

### III.2.E Electrode Separation.

The effect of yield on electrode separation was studied using three different stainless steel counter electrodes (cans) of diameters 1.85 cm, 2.85 cm and 3.45 cm and tapered stainless steel mandrels. Depositions were carried out using a suspension of 100 g of  $\beta - \beta''$  alumina in 200 ml of isoamyl alcohol at 500 v for 1 minute as



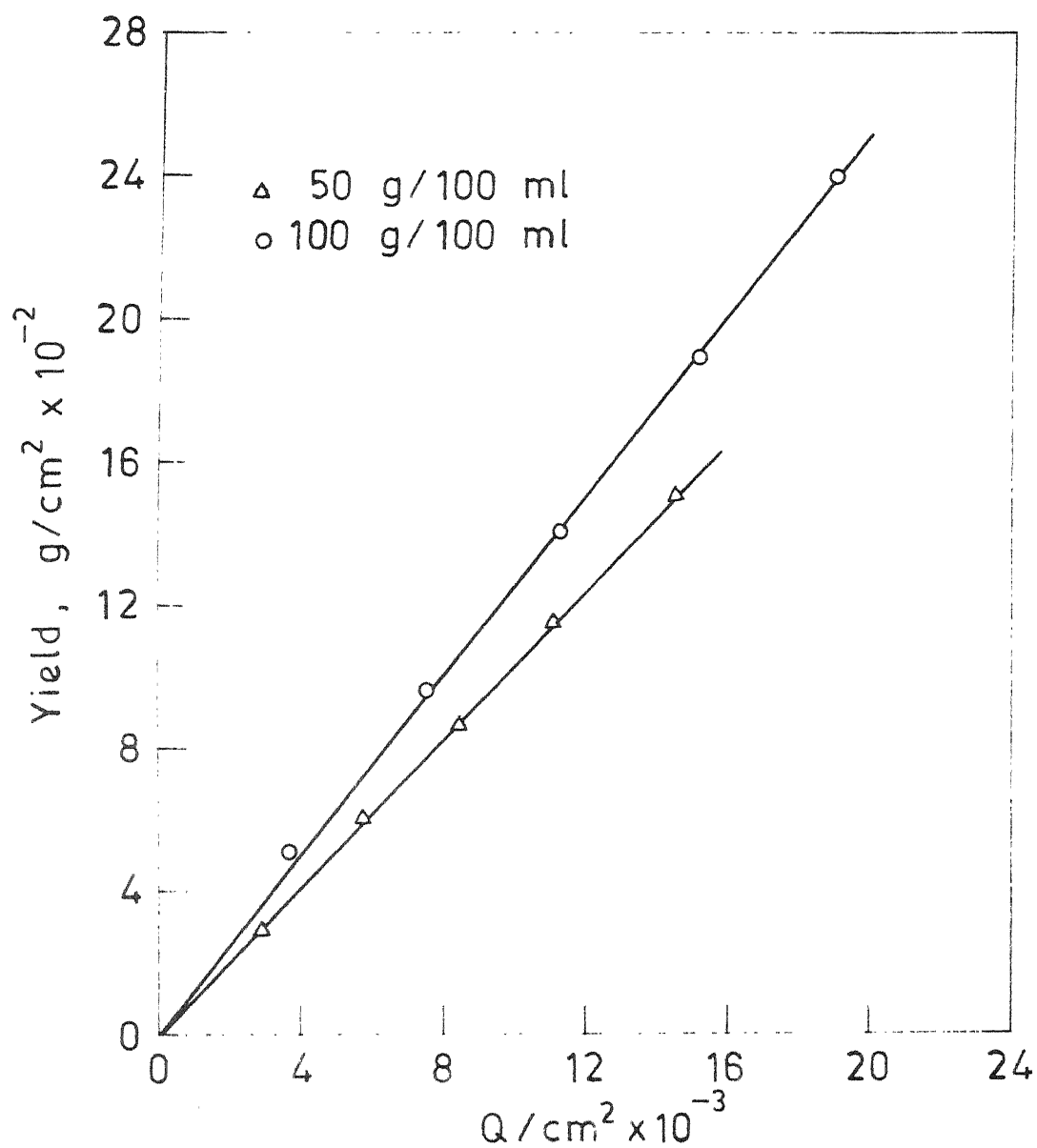


Fig. III.4 Variation of yield with quantity of electricity.

explained in Section II.3.B. The experiments were also carried out at other two concentrations also, using the same suspension after the first set of depositions but the concentration measurement is not done. The yield ( $\text{g/cm}^2$ ) obtained is plotted as a function of reciprocal of  $\ln r_1/r_2$  where  $r_1$  and  $r_2$  are the radii of mandrel and counter electrode in Figure III.5 and the data are given in Table III.2. It was observed that at larger gap, the yield ( $\text{g/cm}^2$ ) is less compared to that at smaller gap. This is because of higher field at small gaps which has resulted in increase in yield and vice versa. On the other hand, according to equation (I.3), the  $\ln r_1/r_2$  term appears in denominator, so when yield is plotted as a function of reciprocal of  $\ln r_1/r_2$ , linear behaviour is observed (within the experimental errors) which was expected. Thus the yield equation (I.3) with respect to changes in depositing cell dimension is verified.

Krishnarao<sup>(17)</sup> has also studied the effect of electrode separation on yield, but the results are expressed as the ratio of the two yields and are compared with theoretical yield ratios calculated using the equation (I.3). It is difficult to plot these yields as a function of reciprocal of  $\ln r_1/r_2$  due to nonavailability of the data.

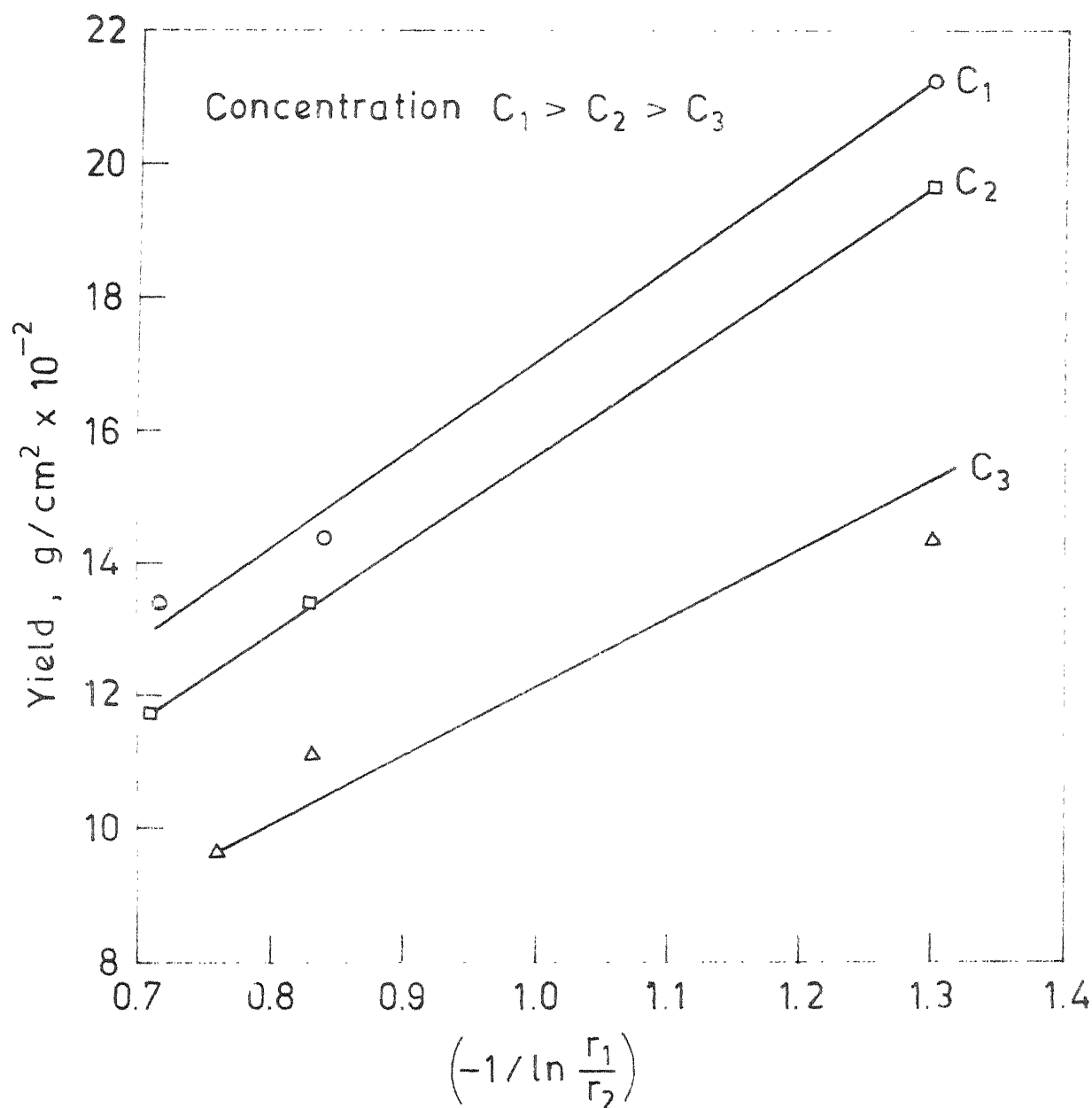


Fig. III.5 Variation of yield with electrode separation at 500 V, for 1 minute, 100 g  $\beta$ - $\beta''$  alumina in 200 ml iso-amyl alcohol.

Table III.2

Data of electrode separation experiment

Concen- tration No.	$r_1$ cm	$r_2$ cm	$\frac{r_1}{r_2}$	$\ln \frac{r_1}{r_2}$	$1/\ln \frac{r_1}{r_2}$	Yield g/cm <sup>2</sup>
I	0.42	1.72	0.25	-1.39	-0.72	13.4
	0.43	1.42	0.30	-1.2	-0.84	14.4
	0.43	0.93	0.46	-0.78	-1.30	21.2
II	0.43	1.72	0.25	-1.4	-0.71	11.7
	0.43	1.42	0.30	-1.2	-0.84	13.4
	0.43	0.93	0.46	0.78	-1.30	19.6
III	0.46	1.72	0.27	0.27	-0.76	9.6
	0.43	1.42	0.30	-1.2	-0.84	11.1
	0.43	0.93	0.46	0.78	-1.30	14.3

$r_1$  and  $r_2$  are the radii of mandrel and counter electrode respectively.

### III.2.F Current-Time Relationship.

In electrophoretic depositions the current should fall in some regular fashion with respect to deposition time. With increase in deposition time, the film thickness increases and hence the resistance at the electrode surface increases. Experiments were carried out using a suspension of 120 g  $\beta$  -  $\beta$ " alumina in 200 ml of distilled isoamyl alcohol in the voltage range of 100-450 V for 1 minute duration maintaining concentration constant in each case as explained in Section II.3.B. The decrease in current was recorded as mV drop across a standard resistance. The current density against deposition time at different voltages is shown in Figure III.6. It was observed that at higher applied voltages the decrease in current is rapid compared to that at lower applied voltage. However, during all the depositions, a sudden increase in current was observed in the beginning of the depositions. This increase was for a very short duration which was difficult to record. This initial increase in current might be because of the movement of the free adsorbed ions present in the suspension, and starts decreasing when the particles begin to get deposited on the mandrel. It was thought that this period of increment in current depends on concentration and voltage. Higher the concentration, the shorter the duration of the increment period. With dilute

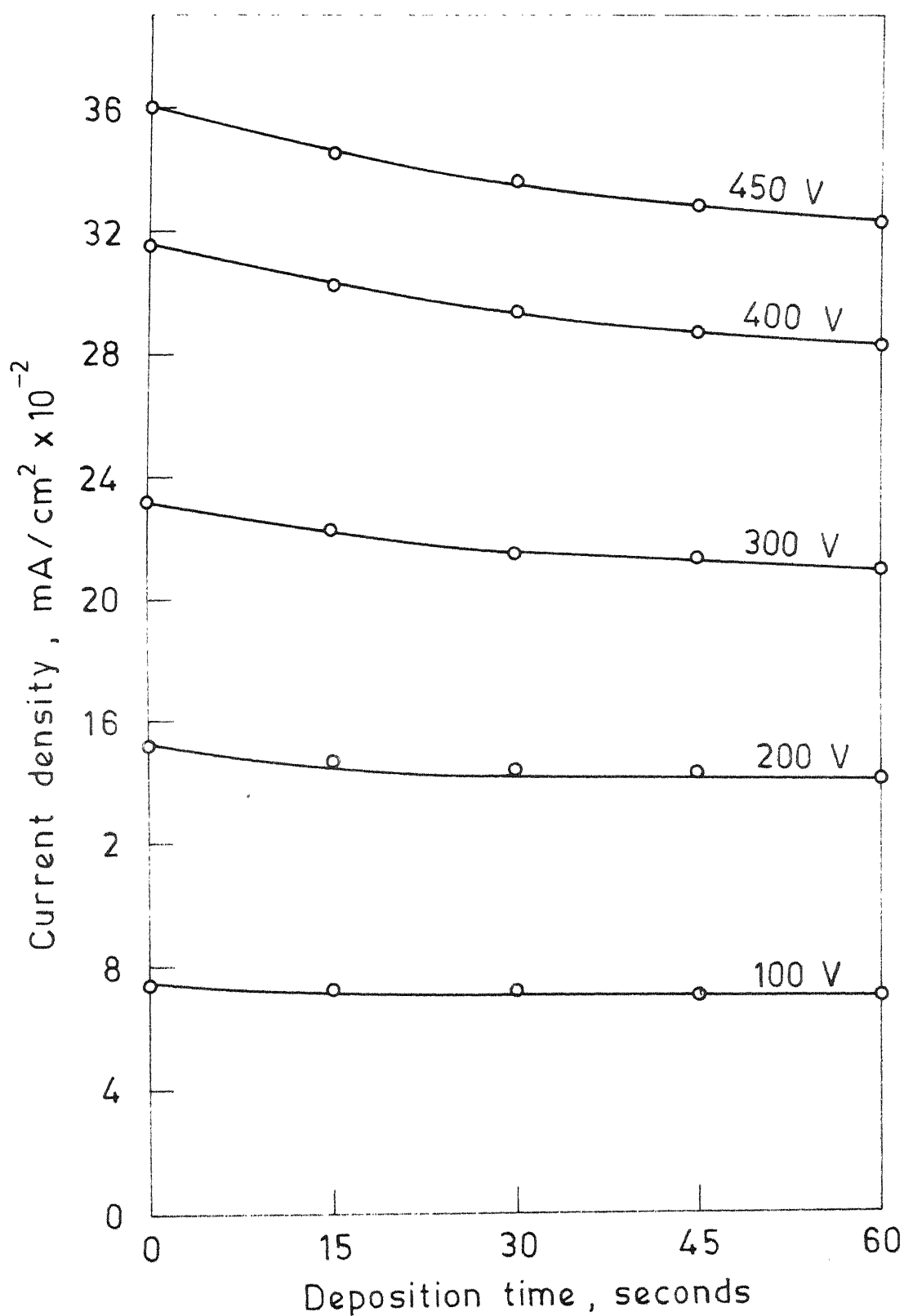


Fig. III.6 Variation of current density with deposition time at different voltages for 120g  $\beta$ - $\beta''$  alumina in 200 ml iso-amyl alcohol.

suspensions and at low applied field this period may get prolonged as particles move slowly towards depositing mandrel. On the basis of this, it was decided to use low concentrations and low voltages for deposition to note the increase in current during the process. For this purpose suspensions with 4 g and 6 g of  $\beta - \beta''$  alumina in 100 ml of isoamyl alcohol was used for two different sets of experiments. The current increased is plotted as mV (since current was measured as voltage drop across a standard resistance) with respect to deposition time (Figure III.7). The lower concentration 4 g/100 ml gave an increment till about 4 minutes and that of 6 g/100 ml gave till about 3 minutes. Hence it is believed that the initial increase in current depends on concentration of the suspension and applied voltage.

### III.3 Deposition of Negatively Charged Particles.

As the aim of the present study is to form the  $\beta - \beta''$  alumina tubes by electrophoretic deposition method, the dried deposits must be removed from the mandrels. Many methods have been tried for this purpose. Powers<sup>(14)</sup> has reported that the long time grinding facilitates in getting negatively charged particles and deposition of these particles on tapered stainless steel mandrels helped him to release the dried deposits. In earlier cases of the

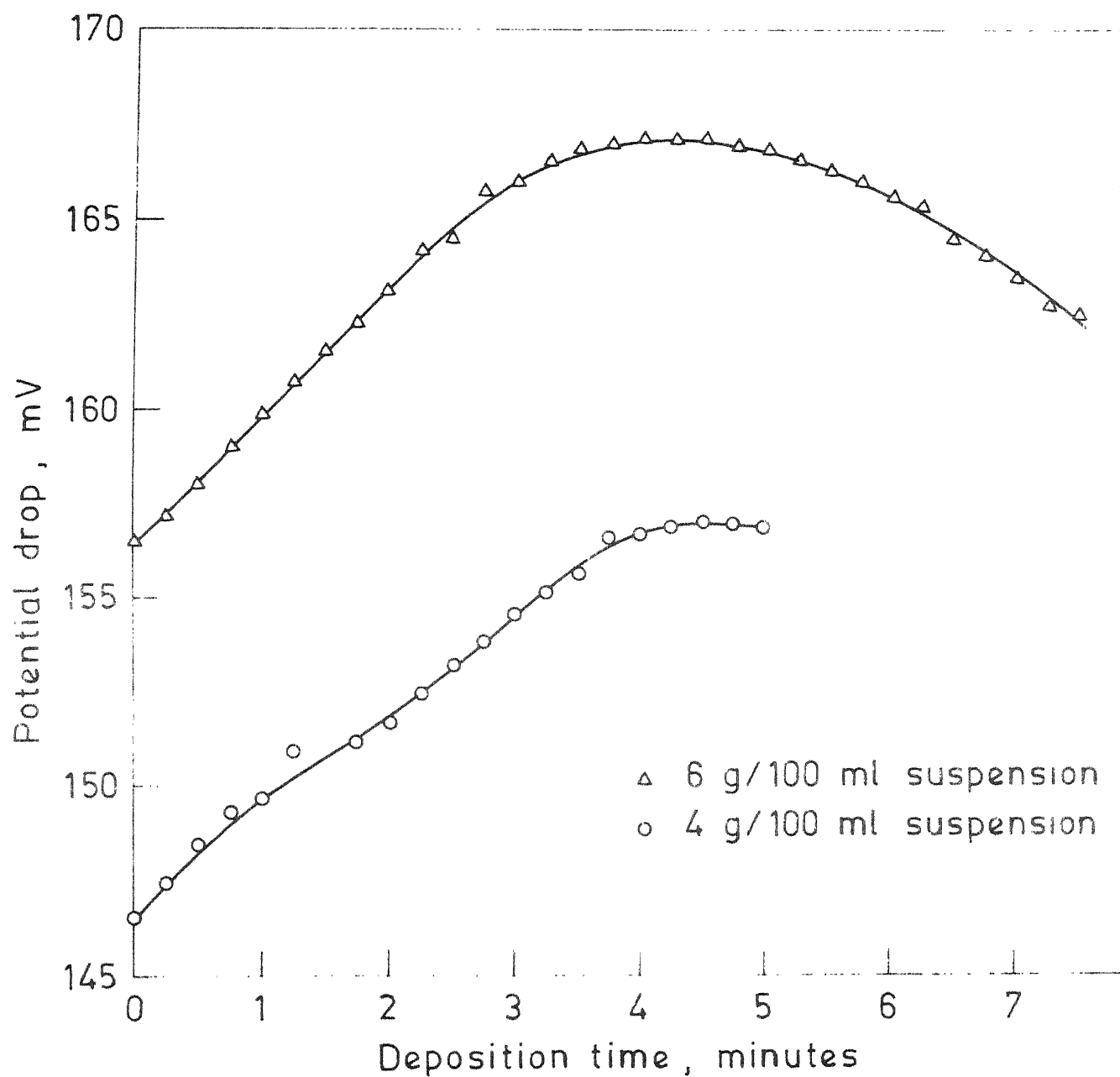


Fig. III. 7 Variation of current at 100 V with deposition time



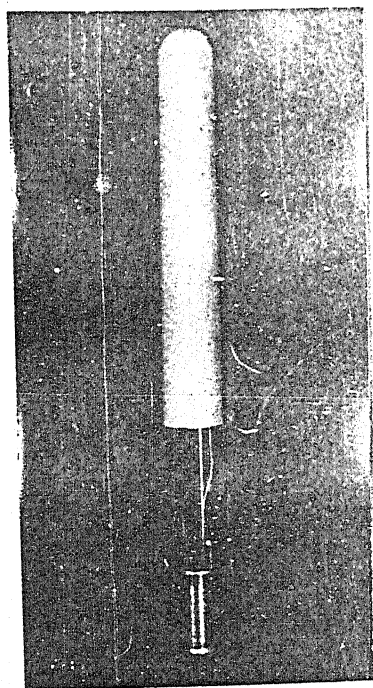
present study with 5 hours of grinding only positively charged particles were obtained, and were deposited over the cathode. But it was difficult to remove the deposits. On the basis of Powers' report it was thought that negatively charged particles really helped him to release the dried deposits after complete elimination of vehicle in-between the mandrel and deposit. The gases  $O_2$  and  $N_2$  which are present in surrounding atmosphere may attract the positive particles to form a coherent bond between the mandrel and deposits. This might be the reason for difficulty in releasing the deposits of positively charged particles. So, an attempt was made to get negatively charged particles. Long time grinding (about more than 20 hours) gave negatively charged particles. These were deposited on anode with 60 g of  $\beta$ -alumina in 200 ml isoamyl alcohol at 500 v for 30 to 60 seconds on tapered stainless steel mandrels. Attempts to remove the dried deposits from the mandrel were unsuccessful. It was not possible to release the deposits without damaging them. So, there is no difference in depositing the positively or negatively charged particles as far as releasing the deposits is concerned. The long grinding times employed by Powers decreases particles size of the negatively charged particles and enabled to get good deposit density.

### III.4 Removal of the Deposits.

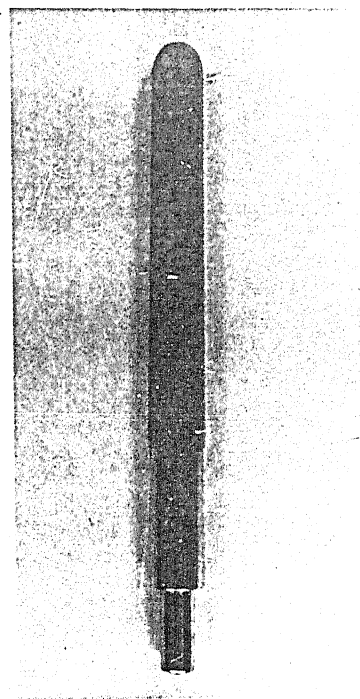
Many other methods were tried to remove the dried deposits from the mandrels according to Section II.3.B. Tapered stainless steel mandrels did not help in this respect and so also the tapered graphite mandrels. Instead of burning the deposited graphite rod as was done by Kennedy et al<sup>(15)</sup>, in the present study an alumina rod with graphite coating over it was employed for the purpose. A uniform graphite coating was obtained with graphite paint in linseed oil medium. Thus the alumina rods with dried graphite coating were used for deposition of  $\beta$  -  $\beta''$  alumina in isoamyl alcohol medium at 500 v for different timings depending on the thickness of the deposits desired. Only qualitative study was made in these cases as experiments were designed to study the relative ease with which deposits can be removed from the mandrels. The graphite layer present in-between the alumina rod and the deposit was burnt off at about 600°C for 30-60 minutes by raising the temperature from room temperature. On cooling to room temperature slowly, cracks were observed over the deposits. In this case CO<sub>2</sub> formed must have increased the pressure between the mandrel and deposit. So the cracks might have formed and through the cracks, CO<sub>2</sub> might have escaped. Kennedy et al<sup>(15)</sup> who burnt full graphite rod at 800°C have not reported any thing about the cracks. The very

slow heating rate (about 20-30°/hour) might help in this respect.

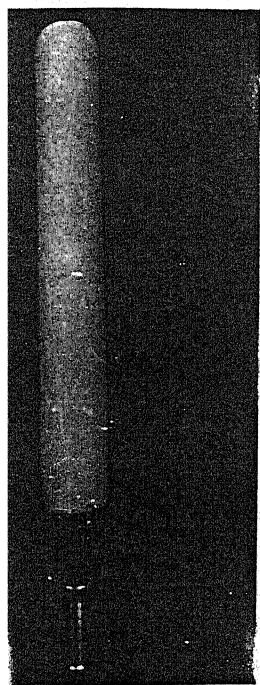
Finally depositions were made on wax layer after coating the wax surface with graphite paint (as explained in section II.3.B), with stainless steel mandrel as support for wax coating. The wax layer can be removed easily in the form of a hollow tube. The depositions made over this were good. The dried deposits were removed along with the wax layer inside the tube from the mandrel. This wax can be removed easily. The photograph of different stages of the deposition on the wax coating is shown in Figures III.8a to III.8d. Figure III.8a shows the stainless steel mandrel with wax coating, Figure III.8b shows the graphite coating over the wax layer, Figure III.8c shows the  $\beta - \beta''$  alumina deposits on wax and Figure III.8d shows the removed deposits along with wax layer inside the deposit. Thus it is easy to deposit  $\beta - \beta''$  alumina on wax layer which facilitates in getting the tubes out. The deposits must be crack free in order to get the tubes completely from the wax layer.



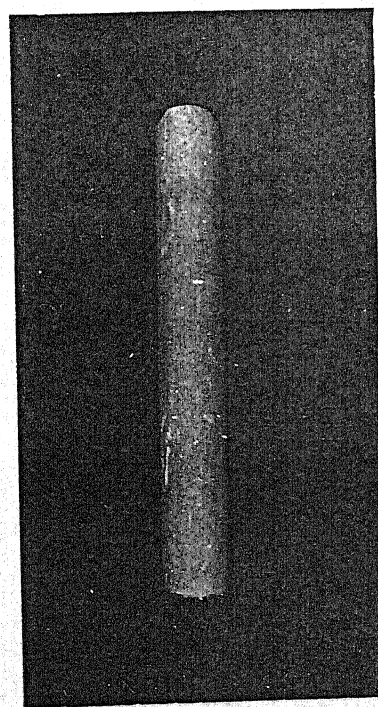
a



b



c



d

Fig. III. 8 Photographs of Deposition on wax coating.

## CHAPTER IV

## SUMMARY AND CONCLUSIONS

Distilled isoamyl alcohol gave reproducible results with  $\beta - \beta''$  alumina suspensions. The kinetic equations suggested by Hamaker and Avgustinik are verified as deposition yield as a function of the following parameters varied one at a time: concentration, deposition time, gap between the electrodes and voltage.

Many methods were tried to get the tubes viz., depositing the powder on tapered stainless steel mandrels, on graphite mandrels, graphite coated alumina rods and on graphite coated wax over tapered stainless steel mandrels. Also, deposition of negatively charged particles on tapered stainless steel mandrels was tried, however this did not help any more and gave almost same type of difficulties for release as that of positively charged particles. Among the other methods tried, depositions on wax gave satisfactory results. It is easy to remove the deposits from the tapered stainless steel mandrels along with wax skeleton.

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## APPENDIX A

To calculate the weight percentage for  $\text{Na}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$ .

Component	Molecular Weight
$\text{Al}_2\text{O}_3$	101.96
$\text{Na}_2\text{O}$	61.98
$\text{Na}_2\text{CO}_3$	105.98
$\text{Na}_2\text{O} \cdot 5 \text{Al}_2\text{O}_3$	571.78

To prepare 100 gm of  $\text{Na}_2\text{O} \cdot 5 \text{Al}_2\text{O}_3$ ,

$$\text{Amount of } \text{Al}_2\text{O}_3 \text{ needed} = \frac{5 \times 101.96}{571.78} \times 100 = 89.16 \text{ g}$$

$$\text{Amount of } \text{Na}_2\text{O} \text{ needed} = 100 - 89.16 = 10.84 \text{ g}$$

$$\text{or Amount of } \text{Na}_2\text{CO}_3 \text{ needed} = \frac{10.84 \times 105.98}{61.98} = 18.54 \text{ g}$$

Total amount of mixture needed for preparation of 100 g

$\beta - \beta''$  alumina

$$89.16 + 18.54 = 107.70 \text{ g}$$



## APPENDIX B

B.1 To find the surface area of the mandrel.

The coated mandrel was weighed and the length of the mandrel over which deposition occurred was measured (SH). The surface area of the mandrel was computed<sup>(17)</sup> using the geometry of the mandrel (Figure A.1) as follows.

$$\tan \theta = \frac{SH/2}{(DX - DI)/2} = \frac{H}{(DO - DI)/2}$$

$$\frac{SH}{(DX - DI)} = \frac{2H}{(DO - DI)}$$

$$\therefore DX = \frac{(DO - DI)SH}{2H} + DI$$

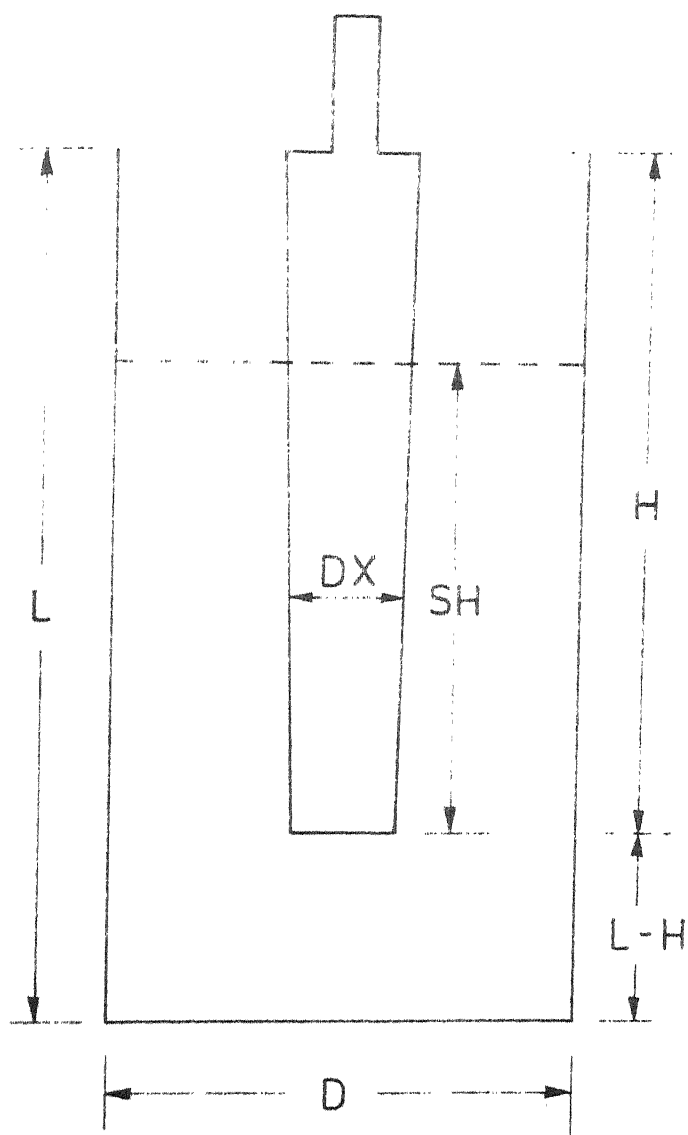
$$\therefore S = \pi DX \cdot SH + \frac{\pi}{4} (DI)^2$$

B.2 Method to find the concentration of the suspension.

The concentration of the suspension was measured as gms of powder per 100 ml of suspension, in a similar way as suggested by Krishnarao<sup>(20)</sup>. It is computed by making use of the geometry of the cell as follows (Figure A.2).

SH is the depth of immersion of the mandrel in the suspension and DX is the mean dia of the mandrel at half level of immersion. The distance apart between the end of the mandrel and the bottom of the can is  $H_1 = L - H$ ,





$$D = 2.85 \text{ cm}$$

$$L = 12 \text{ cm}$$

Fig. A.2 Geometry of the cell.

where L is the depth of the can and H is the full height of the mandrel. Volume of the suspension in the can is

$$V = \frac{\pi D^2}{4} (SH + Hl) - \frac{\pi DX^2}{4} H$$

∴ Concentration of the suspension (gms per 100 cc of

$$\text{suspension}) = \frac{\text{amount of solid in the suspension in gms}}{\text{volume of the suspension in cc}} \times 100$$

B.3 To find the surface area and volume of the suspension at any instant, knowing the height of the mandrel immersed in the suspension, a computer program is made use of, which is shown latter. The mean dia (DX), surface area (SA), volume (V) and distance between the two electrodes (AL) were computed at a distance of every 0.05 cm from the bottom of mandrel to the full length of the mandrel.

B.4 To calculate the amount of solid present in the suspension.

The amount deposited at each deposition was noted and after all depositions, the remaining suspension in the can was dried and weighed. The total amount of solid in the suspension was computed by adding the weight of the remaining dried suspension weight and the total amount deposited. Hence, the total amount of solid present was known at the beginning of the depositions. Now, by just deducting the weight of the deposit of a particular

deposition, the amount left for the next deposition was known. Thus, knowing the amount of solid present at the beginning of every deposition and corresponding volume (calculated by knowing the immersed height of the suspension using computer results), the concentration was calculated. A sample calculation is shown below.

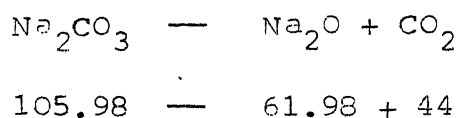
sample calculations (for concentration).

Deposi- tion No.	Height of immersion cm	Vol. of <sup>*</sup> suspension ml	Wt. deposited g	Amount present g	Concen- tration g/100 cc of suspension
1	5.6	66.84	2.09	37.3	55.8
2	5.4	65.7	1.74	35.21	53.59
3	7.2	63.45	2.41	33.47	52.75
4	6.8	61.9	2.07	31.06	50.0
5	6.5	60.1	1.85	28.99	48.2
6	6.3	58.7	1.71	27.14	46.23
7	6.1	57.4	1.6	25.43	44.3
8	5.8	55.9	1.4	23.83	42.6
9	5.6	54.2	1.42	22.43	41.13
			<hr/>		
			16.23		
Wt. of remaining dry suspension			21.07		
			<hr/>		
Total			37.30		

\*From computer result.

## APPENDIX C

To calculate the theoretical weight loss after calcination.



∴ 105.98 g  $\text{Na}_2\text{CO}_3$  loses 44.0 g of  $\text{CO}_2$

∴ 18.54 g  $\text{Na}_2\text{CO}_3$  in 107.7 g of mixture (see Appendix A) loses

$$\frac{44 \times 18.54}{105.98} = 7.7 \text{ g}$$

∴ Percentage loss of  $\text{CO}_2$  is  $\frac{7.7}{107.7} \times 100 = 7.15$

Theoretical loss due to  $\text{CO}_2$  evolution of  $\text{CO}_2$  is 7.15%.

